

*94-1 Research and Development Project  
Lead Laboratory Support*

*Status Report*

*July 1–September 30, 1996*

**Los Alamos**  
NATIONAL LABORATORY

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# **94-1 RESEARCH AND DEVELOPMENT PROJECT LEAD LABORATORY SUPPORT**

**Status Report  
July 1–September 30, 1996**

**Compiled by  
Nora Rink**

## **ABSTRACT**

This document reports status and technical progress for Los Alamos 94-1 Research and Development projects. Updated schedule charts are shown in the appendix.



## EXECUTIVE SUMMARY

This is the fourth status report published for Los Alamos National Laboratory 94-1 Research and Development Project Support. The Department of Energy Office of Environmental Management (DOE/EM) funds these projects in order to support the storage or disposal of legacy plutonium and plutonium-bearing materials resulting from weapons production throughout the DOE complex.

Descriptions and milestones for Los Alamos 94-1 Research and Development projects are found in report LA-UR-96-991, *94-1 Research and Development Project Lead Laboratory Support Technical Program Plan* (April 1996). Figure 1 presents the work breakdown structure for this effort. This document reports status and technical progress for funded Los Alamos 94-1 R&D projects.

This document also serves as an end-for-year review of projects and positions the program for FY97. The technical successes for FY96 are numerous. We begin to apply a number of new technologies to plutonium stabilization problems. Some important successes are as follows:

- successful testing of cryogenic crushing for a glovebox system;
- successful demonstration of salt oxidation for the effective stabilization of pyrochemical salt residues (technology transferred to the Rocky Flats Environmental Technology Site [RFETS]);
- installation of a hydrothermal processing reactor in the Los Alamos Plutonium Facility (TA-55), (awaiting a readiness assessment before treatability studies can begin);
- development of a residue-washing flow sheet for combustibles (work continuing for FY97 to support the RFETS baseline);
- development of experimental protocol for the Shelf-Life Program with input from the newly formed Materials Identification and Surveillance (MIS) working group that consists of representatives from the various sites; and
- core technology activities to develop techniques for x-ray absorption near-edge structure (XANES), extended x-ray absorption fine structure (EXAFS), and plutonium characterization.

As the program moves forward to FY97, we expect changes in the work scope to reflect the conclusions of the Nuclear Materials Stabilization Task Group trade studies on combustible residues and ash residues, as well as to reflect their conclusions on recent discoveries associated with the long-term stabilization of impure oxide. Building on the successes of FY96, the program is well positioned to provide solutions in these and other areas.

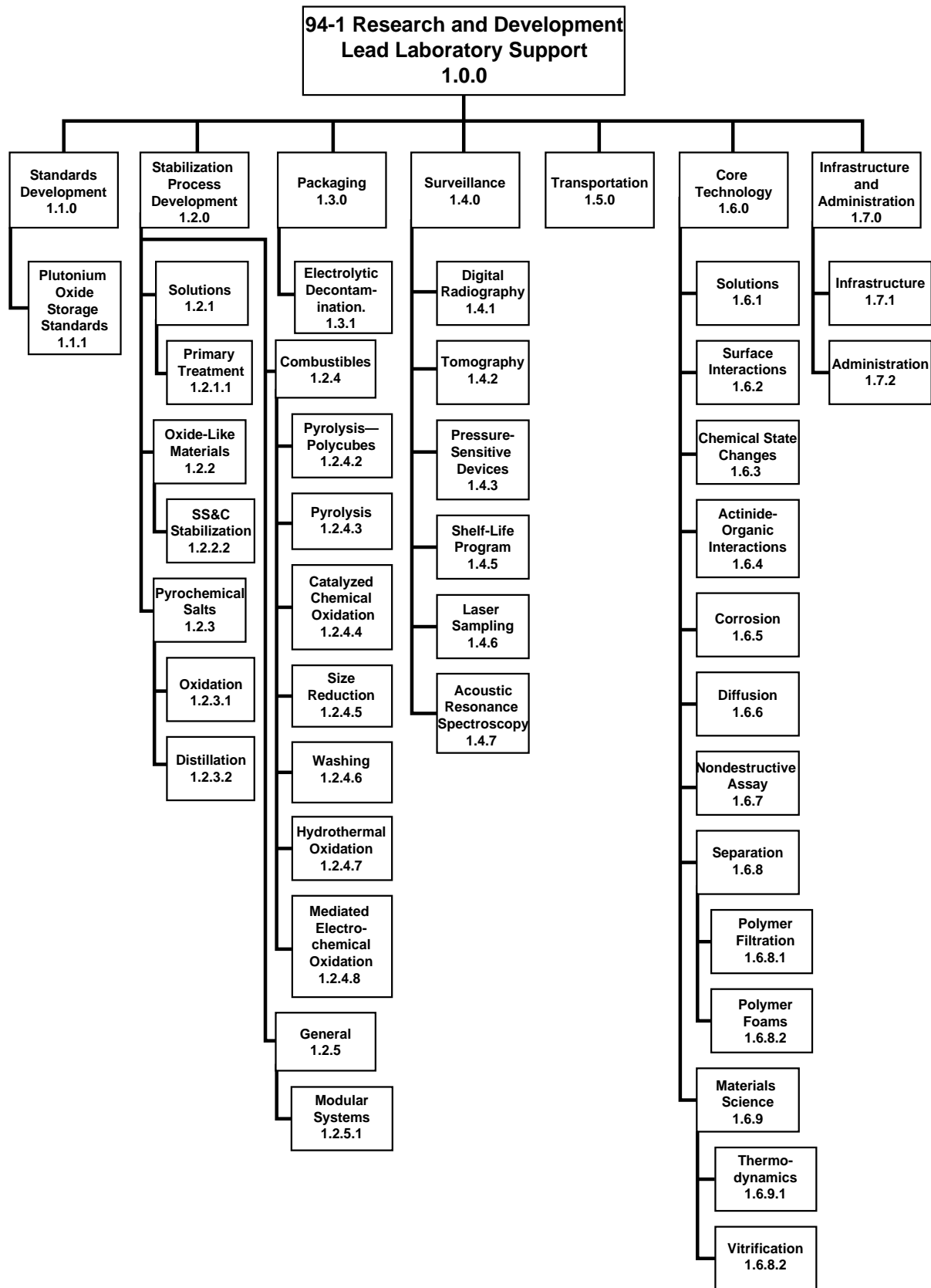


Fig. 1. Work breakdown structure (WBS).

***Sand, Slag, and Crucible Stabilization: High-Gradient Magnetic Separation***  
**Principal Investigator: Laura Worl**

**Task Description.** Los Alamos National Laboratory personnel will use magnetic separation techniques to test sand, slag, and crucible (SS&C) residues for plutonium removal and concentration. The goal is to demonstrate the production of a plutonium-concentrated stream and a plutonium-deficient stream from SS&C. The work described here was funded for nine months of FY96.

SS&C residues, stored at DOE facilities, are contaminated with plutonium. In some cases, the residues have 10%–20% plutonium content. Westinghouse Hanford Company (WHC) has 4300 kg of SS&C residues that have been targeted for treatment and disposal by dry processing. Concentrating the plutonium into a rich fraction would allow a smaller inventory of residues to be shipped to sites, such as the Waste Isolation Pilot Plant, and would aid the recovery of plutonium for long-term storage.

**Status/Accomplishments.**

**Experimental.** We obtained several Los Alamos SS&C samples from the storage vault. We either directly processed the residue on the magnetic separator or dry sieved it in order to obtain a more uniform particle size distribution. The sized particles were placed into a hopper that was fitted with a feed chute that has an adjustable feed rate. Feed rate through the chute is determined by a combination of vibration amplitude

and particle size of the feed material. The feed is deposited on the moving belt, and the particles are passed through the magnetic field created by the magnetic roll. The force exerted on the particles causes the paramagnetic particles to remain in contact with the belt, while the diamagnetic particles experience a repulsive force from the belt. The splitter bar acts as a divider between the diamagnetic plume coming off the belt and the paramagnetic tails that are collected in the catch trays beneath the belt. We weighed the trays and emptied their contents into sample containers.

Approximately 10 samples per experimental run were collected. We then removed the samples from the glovebox line through a bagout procedure and sent them for analysis. Measurements of all sample activity were obtained with gamma spectroscopy.

The roll separator performance is affected by several variables such as particle size, feed rate, belt speed, splitter plate settings, belt thickness, and magnetic-field strength and gradient. The magnetic-field strength, field gradient, and belt thickness are fixed for a given separator; and we did not vary them in the experiments.

A uniform feed particle size is important in eliminating particle interference and is achieved by dry sieving. We dry sieved the residues



with 600- $\mu$  (30-mesh) and 106- $\mu$ (140-mesh) sieves. Only the material between the two mesh sizes was processed with the separator. The separator feed rate is important because too much material layered onto the belt will not permit the particles to experience the full magnetic-field strength. We adjusted the feed rate to deposit the particles onto the belt in a relatively thin, even layer in order to maximize separation. For a given feed setting, the feed rate is dependent on particle size, with larger particles tending to feed onto the belt at a faster rate.

Belt speed is a variable that is also crucial to an effective separation. The belt speed determines the centrifugal force experienced by the particles. This centrifugal force counteracts the magnetic force and allows the diamagnetic particles to be projected off the front of the magnetic roll. The paramagnetic particles that stay on the belt longer are deposited under the magnetic roll and behind the splitter plate. The splitter bar setting determines how the separated fractions of paramagnetic and diamagnetic particles are collected in the catch trays. We used a qualitative method to set the splitter bar.

The variability of the feed, the feed rate, the particle size, and the belt speed made it difficult to have a predetermined splitter bar setting. We set the splitter bar position only after the feed was already coming off the belt and we could observe the plume. A well-defined magnetic tail can be

observed as the material exits off the front of the belt. We set the splitter bar to capture this magnetic tail.

Belt thickness influences the magnetic-field strength on the particles. The thinner the Kevlar™ belt, the higher is the magnetic field available to the particles and the more effective is the separation between paramagnetic and diamagnetic components. Therefore, a thicker belt will result in a decrease in performance. The drawback to a thinner belt is a shorter belt life. In our studies we used a 0.005-in. Kevlar belt.

**Results.** We tested three SS&C residues from the Los Alamos inventory. The residues were identified as follows:

- MAG-26: Residue used in previous open gradient magnetic separation (OGMS) tests performed at Los Alamos;
- SSC-490: SS&C residue sized at  $-600\ \mu\text{m}$  and  $+106\ \mu\text{m}$ ; and
- SSC-481a: higher-activity SS&C residue sized at  $-600\ \mu\text{m}$  and  $+106\ \mu\text{m}$ .

A summary of the test results during this period appears in Table 1. The table includes concentrations of the feed, lean and rich streams, and a performance metric concentration ratio (CR), defined as the activity fraction of the rich stream divided by the mass fraction of the rich stream. The higher the concentration ratio, the better is the separation. In general, ratios exceeding 1.5–1.7 are of practical importance.

**Table 1. Summary of Magnetic Separation Tests on Sand, Slag, and Crucible**

Run	Belt Speed (rpm)	Feed Rate (setting)	Feed Concentration (% Pu)	Lean Concentration (% Pu)	Rich Concentration (% Pu)	Concentration Ratio*
30-MAG-26R	250.0	5.5	1.45	0.56	2.66	1.8
31-MAG-30L	150.0	5.5	2.65	1.18	3.45	1.3
31a-MAG-30R	280.0	5.5	0.53	0.55	0.05	1.1
32-MAG-30L	150.0	5.5	2.62	1.76	3.02	1.2
33-MAG-26R	120.0	5.5	2.41	1.09	2.83	1.2
34-SCC-490	100.0	5.5	4.51	2.45	15.62	3.5
35-SCC-490	80.0	5.5	4.39	1.94	7.51	1.7
36-SCC-490	100.0	5.0	5.27	3.93	7.32	1.4
37-SCC-481a	100.0	4.5	22.7	19.4	27.12	1.2

\* Concentration ratio is the plutonium concentration of the rich stream divided by the plutonium concentration of the feed stream.

We performed five magnetic separation tests on MAG-26. These results have been discussed in the earlier quarterly reports. In summary, results from this series of runs indicated that a scalping pass at high belt speed would remove any nonradioactive magnetic material present. This scalping pass was then followed by a low-speed pass in order to allow collection of the magnetic contaminant in the magnetic fraction.

In runs 34–36 we examined SS&C residue SCC-490. All three runs included a high-speed scalping pass to remove any magnetic mineral present. In the scalping pass, the high-density actinides reported to the nonmagnetic fraction as a result of the large centrifugal force. We then further processed the nonmagnetic fraction at lower belt speeds and feed rates in order to remove the actinides from the nonmagnetic components. We

obtained the best results in run 34 (CR = 3.5) at a belt speed of 100 rpm and a feed rate setting of 5.5. Run 35 was processed at a lower belt speed and Run 36 was processed at a lower feed rate. Both of these adjustments resulted in decreased concentration ratios.

We obtained a richer SS&C residue (SSC-481a) from the Los Alamos vault in order to determine whether the roll separator is effective on materials with higher concentrations of plutonium. As in previous runs, we performed a scalping pass at 350 rpm in order to remove any magnetic mineral present. The lean fraction, which contained most of the activity, was then processed at 150rpm. Approximately 23% of the mass and 28% of the activity moved to the magnetic fraction, while 69% of the mass and 59% of the activity moved to the nonmagnetic fraction. The balance of

the material was reported as middlings. This pass resulted in a concentration ratio of 1.2, which is similar to results we obtained with the leaner residues.

***Discussion and Conclusions.*** This investigation is an extension of previous work on the magnetic separation of dry residues. In previous investigations we showed OGMS to be effective in isolating paramagnetic contaminant plutonium from graphite and SS&C residues. However, the processing rates were relatively low at 0.1kg/h. In order to increase processing rates, we investigated the use of a rare-earth magnetic roll separator. This device is based on permanent magnet technology, and therefore is somewhat easier to implement, especially in a glovebox environment. We found residues with strongly diamagnetic properties, especially graphite, to be highly separable when we used the rare-earth roll separator. However, in those previous investigations, SS&C residues showed poor treatability.

In this present investigation, we undertook a systematic approach to

address the SS&C residues. This approach included optimizing feed rate, belt speed, and splitter bar position. In addition, we dry sieved feed samples in order to provide a more uniform particle size. Results from this investigation are significantly better than from investigations performed by the previous roll-separator on SS&C residues. Plutonium concentrations were enriched to greater than 15% from feeds of 4.5%, and plutonium concentrations as low as 0.5% were achieved from feeds of 1.5%.

The rare-earth magnetic roll separator is a relatively simple and inexpensive device that is well suited for glovebox use. It can have a processing rate as high as 200 g/min, which is significantly greater than the rate achieved with other OGMS systems. If the contaminants are physically liberated in the feed material, which was not the case for the SS&C residues tested in this investigation, a high degree of separation can be achieved. The roll separator appears to be most effective for particle sizes greater than approximately 100  $\mu\text{m}$ .

***Pyrochemical Salts: Salt Oxidation***  
**Principal Investigator: James McNeese**

**Task Description.** The purpose of the salt oxidation task is to demonstrate treatment methods to oxidize wet or reactive pyrochemical salts. Treatment methods are necessary in order to satisfy the near-term Defense Nuclear Facilities Safety Board (DNFSB) 94-1 schedule for reducing, within three years, the risk of potentially unstable residues. Our objective is to develop and transfer to Rocky Flats Environmental Technology Site (RFETS) process technology that will stabilize reactive metals contained in these pyrochemical salts and that will prevent dangerous levels of hydrogen gas generation during storage.

**Status/Accomplishments.** Los Alamos National Laboratory researchers in collaboration with RFETS personnel developed a chemical oxidation process that uses sodium carbonate as the oxidant. This process has been shown to be effective in stabilizing pyrochemical salt residues.

One safety concern with unstabilized spent pyrochemical salts is the potential for reactive metals to be in the salt residue. These metals can react with water to form hydrogen; and, if the metal is finely divided, pyrophoric behavior is possible. The oxidation process is based on the chemical oxidation of reactive metals by carbonate. The carbonate is soluble in the pyrochemical salt matrices when they are molten. The soluble carbonate reacts with metallic species in the salt

and oxidizes them to the metal oxide. This process is particularly useful in converting alkaline and alkaline earth metals to oxides. Actinide metals and their chlorides are also converted to oxides using carbonate oxidation.

The effectiveness of the stabilization process is measured by the amount of gas evolved from the matrix after treatment. During the process development effort, we measured, before and after treatment, all the feed salts for gas evolution. An added benefit of the oxidation process is that the processing sequence will remove all the sorbed water that could be in the matrix from extended storage. Reducing the water level to the lowest possible level during the oxidation process will minimize the amount of corrosion from salts that are stored after treatment.

The oxidation process is a simple, robust process that is effective for the majority of pyrochemical salt residues stored at RFETS and at Los Alamos. Los Alamos personnel developed process parameters for molten salt extraction (MSE), electrorefining (ER), direct oxide reduction (DOR), and salt strip (SS) salt residues. The process parameters developed are specific to the type of residue salt matrix being treated. The amount of carbonate added varies from 2.2 g carbonate per gram plutonium for the MSE salts to 50 g carbonate per kilogram of bulk salt for the DOE salts. The amount of

carbonate required is sufficient to oxidize all of the reactive metals to oxide and also to convert the actinide species (both metal and chloride) to the oxide. This fact allows further processing, such as salt distillation, for the MSE, ER, and SS salts, if actinide separation is deemed necessary. The DOE salts would be suitable for water dissolution of the calcium chloride with filtration recovery of the actinide oxide.

The developed oxidation process can be accomplished in standard stationary pyrochemical furnaces (used at Los Alamos and RFETS) with minimal changes to the furnaces. An added benefit arising from the process development effort is that the process can be performed in reusable stainless steel reaction crucibles. This factor will greatly reduce the amount of transuranic waste that would arise from the use of ceramic crucibles. The process can also be accomplished

easily in an 8-hshift with one run per furnace per shift and by active cooling of the reactor contents, if an accelerated process is necessary.

Analysis of the gas evolved from the feed salt samples by mass spectroscopy shows that the gas formed from water dissolution is predominantly hydrogen. From this fact, we understand that stabilization will minimize the amount of hydrogen that can arise from the stored salts should they be exposed to water. Analysis of the gases evolved during the processing shows concentrations above background levels of hydrogen, methane, carbon monoxide, and carbon dioxide. Each of those gases are well below levels that could cause combustion or an explosion, and no gas treatment is necessary before release to the atmosphere, other than the normal high-efficiency particulate air (HEPA) filtration for glovebox exhaust.

***Pyrochemical Salts: Salt Distillation***  
**Principal Investigator: Eduardo Garcia**

**Task Description.** The salt distillation process is designed to separate plutonium pyrochemical salts into a very lean fraction of the total (<100 parts per million [ppm] plutonium) and plutonium oxide suitable for storage under DOE Standard 3013. The chloride content of the pyrochemical residues is thereby converted into stable, slightly contaminated salt; and the plutonium content is separated into a homogeneous, well-characterized, oxide material suitable for long-term storage.

**Status/Accomplishments.** During the fourth quarter of FY96, Los Alamos National Laboratory personnel completed testing using uncontaminated salts. We disassembled the equipment and placed it into a glovebox. Tasks completed during this period include nonradioactive testing of production-scale equipment, hardware installation, and environment, safety, and health (ES&H) compliance activities. We also partially completed operator training for testing with radioactive materials. The activities required to complete these tasks included completion of a final design report, introduction of the equipment into the glovebox, glovebox modifications for utilities and feedthroughs, review of the process for compliance purposes, and establishment of authorization for beginning of operations.

Once the equipment was reassembled in the glovebox, we tested it with uncontaminated salt in order to confirm that operations would proceed as expected based on results of tests conducted in a nonradioactive laboratory. Results on uncontaminated salts confirmed expected behavior and we proceeded to test salts containing plutonium. For the first test, we melted 2 kg uncontaminated sodium chloride-potassium chloride salt with 50 g plutonium oxide. This feed was then run through the process that is now standard.

The run proceeded normally and a dry, pourable powder was obtained as the distillation heel. The weight of this powder was 51.4 g. The weight gain may be the result of residual plutonium from the crucible or from the stirrer used in preparing the test salt. No chloride analysis is yet available, so we cannot rule out incomplete removal of the salt. Analysis of a distillate salt sample was very encouraging. We decided to contain a plutonium concentration of 0.037ppm plutonium and 0.0018ppm americium. This concentration is almost two orders of magnitude below the low-level waste (LLW) criterion. Although this result is preliminary and was not obtained with an actual residue salt, it leaves no doubt that the equipment is capable of producing salts that meet the LLW criterion.

Test results have been so good that we will now begin to use residue salts as test feeds. If tests with residues continue to provide results that are as

good as those of previous experiments, we can begin routine production-scale demonstration processing in October 1996.

***Pyrochemical Salts: Measurement of Moisture in Pyrochemical Salts***  
**Principal Investigator: L. C. Baylor, Savannah River Site**

**Task Description.** Thousands of kilograms of plutonium-bearing pyrochemical salts have been designated as needing conversion to a more stable, lower-risk form. Personnel at Los Alamos National Laboratory are developing technology to stabilize reactive metals in the salts and to minimize corrosion caused by the presence of moisture. In situ measurement of moisture content will aid in control of the stabilization process. Personnel at the Savannah River Technology Center (SRTC) have experience measuring moisture by remote fiber-optic near-infrared (NIR) spectroscopy. This experience will be used to develop a system to perform this measurement.

**Status/Accomplishments.** Savannah River personnel will meet with Los Alamos project leaders in mid-

October 1996. The results of this meeting point to a possible redirection of this project from working with moisture in plutonium-containing salts to working with moisture in plutonium oxides. SRS principal investigators are awaiting further guidance before proceeding with tests on substitutes for radioactive materials.

The new lead/sulfur (PbS) NIR diode array spectrophotometer did not perform up to expectations and was returned to the vendor for evaluation. The vendor discovered a crack in the detector housing and repaired it. Return of the unit to SRS is expected soon. The performance of this instrument and our existing NIR diode array spectrophotometer will be compared on substituted materials.



<b><i>Combustibles: Pyrolysis—Polycubes</i></b> <b>Principal Investigator: Daniel J. Kathios</b>
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**Task Description.** To perform criticality studies, personnel at various sites in the nuclear weapons complex manufactured plutonium and uranium oxides that were cast in a polystyrene matrix. Approximately 1600 such polycubes in storage at Westinghouse Hanford Company (WHC) are now a waste that is not suitable for long-term storage.

Pyrolysis is a pyrochemical technique whereby a high-temperature inert environment is used to break down and volatilize polymeric materials. The aim of this work is to design, test, and implement a pyrolysis system that will effectively destroy and remove the polystyrene matrix, leaving the oxides as free-flowing powders that are suitable for either dissolution or long-term storage.

**Status/Accomplishments.** Tests with nonradioactive materials have shown that the Los Alamos National Laboratory pyrolysis reactor design allows for almost 100% removal of the polystyrene without the formation of tars or other constituents that could adversely affect reactor operation. After the pyrolysis operation, we will use an off-gas treatment technology to oxidize the organic constituents. Los Alamos National Laboratory researchers will consider secondary combustion, catalytic conversion, and silent discharge plasma (SDP) for treatment of the pyrolysis off-gas. The polycube pyrolysis system will operate

in compliance with environmental and safety regulations and will be suitable for glovebox operations. The pyrolysis system must be delivered to WHC to process the remaining inventory of polycubes.

In the fourth quarter of FY96, Los Alamos personnel ordered the materials and began fabrication of the pyrolysis units. The pyrolysis reactors should be ready for assembly in November 1996. In July we conducted a project review with WHC personnel. At that time we were directed to develop the process for a two-furnace, two-cube-per-furnace operation that would have a 99% efficiency in destroying and/or in removing materials from the off-gas that do not meet air quality standards. Principal investigators and project personnel reviewed the polycube engineering study prepared by WHC. WHC selected SDP as the preferred off-gas treatment technology option.

Los Alamos released a subcontract to Science Applications International Corporation to provide hazards analysis expertise. Principal investigators developed a bounding accident scenario for the polycube process and a scheduled a process-hazards analysis session was scheduled for October 1996.

Los Alamos personnel released the subcontract for the design of the secondary combustion unit, and

T. K. Thompson, Inc., began the final design of the unit. The design and procurement specifications are scheduled for completion in November and December, respectively.

Several studies were conducted on the SDP unit to determine whether film formation on the walls of the unit could be inhibited while we operated the cells at higher temperatures. The results of these studies indicated that the film was much less tenacious, was harder, and could be easily removed from the SDP walls, if the SDP cell was operated without polystyrene feed.

Los Alamos personnel prepared a summary of system requirements for the WHC project authorization request. We calculated several energy

balances in order to investigate the potential temperature increases when the pyrolysis off-gas “pulse” is oxidized in the off-gas treatment systems. This pyrolysis off-gas “pulse” presents significant thermal and operating challenges for all three treatment technologies.

Los Alamos personnel received the catalyst for the catalytic conversion units and also ordered and received the construction materials for the reactors. Fabrication was begun. Testing of the catalytic conversion system will begin in January 1997.

We also began assembly of the B-Line Strut™ system for the WHC polycube stabilization system and initiated procurement of the control system for the polycube stabilization system.

## ***Combustibles: Catalytic Chemical Oxidation***

**Principal Investigator: Charles Brown**

**Task Description.** The object of this task is to demonstrate the catalytic chemical oxidation technology, specifically the DETOX<sup>SM</sup> process patented by Delphi Research, Inc., (DRI) of Albuquerque, New Mexico. The task includes the following major activities:

- design and configure the demonstration unit to provide a system ready for glovebox installation in the Los Alamos National Laboratory Plutonium Facility (TA-55),
- continue to evaluate final disposition of liquid effluent and spent DETOX reaction solution, and
- install and test the demonstration system on combustible plutonium residues.

**Status/Accomplishments.** DRI completed the preliminary design report in July. This report was included as part of a package initiating the safety and authorization review process at Los Alamos. Higher priority projects at TA-55 have delayed the safety review for the catalytic chemical oxidation system until the first part of FY97. Project personnel are working with TA-55 management to move this project to a higher priority. A glovebox at Rocky Flats Environmental Technology Site has been identified as a possible backup, if

we cannot run the demonstration at Los Alamos by an appropriate time.

We have ordered all the equipment and parts. Construction of the mock glovebox at DRI has been completed. DRI and Los Alamos personnel have identified the needed feedthroughs for the glovebox. We have begun equipment installation in the mock glovebox and have completed assembly of the gas vent system. Also, we have begun assembly of the coolant system, gas supply system, and control system.

Delivery of the tantalum-lined reaction vessel and reflux condenser is being delayed because of difficulty in obtaining tantalum stock. The reason for this delay is that the two major U.S. companies producing tantalum stock both closed down their tantalum mills over the summer in order to allow orders to accumulate. The projected delivery date for these parts is now October 31, 1996. As far as we know, we can take no reasonable action to speed up this schedule, so assembly of the glovebox unit will be about one month later than we originally estimated.

We have demonstrated hydrolysis of ferric chloride in a DETOX solution to form iron oxide ( $\text{Fe}_2\text{O}_3$ ). The process involves two steps. At about 160°C, ferric chloride hydrolyzes to the oxychloride ( $\text{FeOCl}$ ). This first step is complete at about 190°C. The second

step is run at about 200°C. A fine water spray (or steam) hydrolyzes the oxychloride to form  $\text{Fe}_2\text{O}_3$ . Completion of the reaction's second part is slow, mostly because uniformly dispersing the very small amount of water used at this scale is difficult. Steam seemed the most effective approach. Before we can complete the engineering design, we must optimize construction material, water or steam addition, and heating technique.

The final solids contain less than 1% chloride. They are crumbly, relatively coarse, and easy to wash and to filter, if required. We believe that when temperature is controlled at or below 200°C, plutonium chloride and most other chlorides will not hydrolyze, although we have not yet demonstrated this parameter. It is possible that plutonium chloride could be washed out of the iron oxide as a method of dispositioning the plutonium.

### ***Combustibles: Cryogenic Size Reduction***

**Principal Investigators: Timothy O. Nelson and Horacio E. Martinez**

**Task Description.** Cryogenic grinding at low temperature reduces materials in size. However, some materials can be processed at room temperature and still meet processing requirements.

**Status/Accomplishments.** During a visit to the Franklin Miller Facility in Livingston, New York, in July, Los Alamos National Laboratory personnel ran some soft waste through a Task Master™ shredder, similar to the model on order for the Cryogenic Size Reduction project. In doing so, we learned several things, for example:

- Polyethylene bottles will need to be pushed into the cutting blades.
- Blades cut better if material is not folded.
- There was no flyback of the material during shredding.
- Rubber gloves probably need to be cooled in liquid nitrogen (LN<sub>2</sub>).
- Brass zipper pulls may get wedged between the blades, so a switch on the machine should be adjusted so as to turn the current limiting down. The zipper itself should run through the shredder.
- The Task Master shredder can be ordered with small cutters on one side and large cutters on the other, and a sizing mesh can be ordered so that larger material will be pulled around the outside of the blades and be recut.

The Task Master is a quiet machine with little vibration. The unit ordered will weigh about 300 lb. It is easy to clean. Blades cut in a scissors-type action and wear on the inside surface, not on the teeth. The lifetime of the blades is estimated at 1 year with 40-h-per-week operation. Blade wear can be checked by the amount of current being drawn and by the way the material is cut up. The shredder can be modified easily to fit into a glovebox and will safely operate in a glovebox with simple safety interlocks. It appears that the shredder we ordered will reduce the size of material enough for it to be used on the hydrothermal project.

The Los Alamos Photo-Video group will make a video of the cryogrinding equipment. The video will describe the LN<sub>2</sub> introduction system and the filter shredder, cryo compactor, and low-speed shredder. We have reviewed the script for technical content, and filming will begin as soon as the shredder is delivered in October 1996.

We have begun plans for modification of the shredder. The cutter housing inside the glovebox and the gearbox and motor outside the glovebox will be connected through the glovebox wall by means of a drive shaft and a rotating seal. We will determine the exact configuration when we locate a glovebox to house the grinding system. We will run typical soft wastes through the shredder and perform

particle-size analysis. The shredded material will then be given to the

hydrothermal team to see whether a sizing mesh will be required.

**Combustibles: Washing****Principal Investigators: Norman C. Schroeder and Moses Attrep**

**Task Description.** The objectives of this task are (1) to test a proposed process flow sheet for a process designed to remove organics (cutting oil), solvents (carbon tetrachloride [CCl<sub>4</sub>]), and finely divided plutonium from combustible residues and (2) to stabilize the plutonium. The project is divided into two portions: working with nonradioactive cerium substituted materials and experimenting with plutonium-containing materials. Presently, the focus of this task is to demonstrate desorption and plutonium stabilization unit operations.

**Status/Accomplishments.** Additional work was done with nonradioactive wet combustible material at Rocky Flats Environmental Technology Site. We documented the behavior of cerium metal in a variety of cases. We conducted 10 experiments in order to investigate the oxidation of cerium metal turnings that have been coated with cutting oil. The cutting oil was a 50/50 mixture of Texaco Transultrex A and H cutting oils. We conducted experiments using a GlasCol 2-L reactor, open beakers on a hot plate, and a Parr reactor. These experiments provided useful data and developed the techniques needed for the subsequent plutonium metal oxidation experiments.

We have found the following:

- Oil-coated cerium can be oxidized with water at atmospheric pressure, but the reaction proceeds slowly.
- Oxidation of oil-coated cerium is enhanced in a pressurized system (Parr reactor) because the operating temperature is higher and the partial pressure of water (the oxidant) is higher. However, the oxidation rate may be too slow to convert the quantities of metal required in the allocated time of 1–1.5 h. Hence, we searched for agents that would enhance the process.
- Sulfamic acid enhances the oxidation rate of oil-coated cerium metal to its oxides more than hydrogen peroxide does.
- The amount of oil-coated cerium oxidized in the presence of sulfamic acid seems to be relatively independent of the amount of added 1 M sulfamic acid. The exact role of sulfamic acid is unclear at present. The amount of sulfamic acid added to the quantities of cerium metal are substoichiometric.
- Within 2 h, up to 4 g of oil-coated cerium metal can, in the presence of sulfamic acid, be converted to oxides.

We have determined that water-saturated material (no free water) is approximately a 1:1 (volume to weight) of water to material. This information is important if complete wetting of the sample is required, especially if sulfamic acid must come in contact with the metal pieces.

Plans and activities are continuing for installation of the Parr reactor in the glovebox in the Alpha Facility at the Los Alamos National Laboratory Radiochemistry Site (TA-48). We anticipate the delivery of the Parr reactor for the glovebox in October. Final preparations of the glovebox and safety assessment are continuing while we await delivery of the reactor. Plutonium turnings are expected to be delivered in early October 1996.

We will conduct a few additional experiments that use the sulfamic acid

system. We will determine the following:

- whether sulfamic acid has to be in direct contact with the metal in order to enhance the oxidation;
- what effect the sulfamic acid has on the cerium and the resulting oxidation of the metal;
- what effect the presence of carbon tetrachloride has on the sulfamic acid system; and
- what limiting amount of sulfamic acid is needed to effect rapid oxidation.

In early 1997 we will be completing plans for installing the Parr reactor and designing experiments for plutonium oxidation in this reactor.



### ***Combustibles: Hydrothermal Oxidation***

**Principal Investigators: Laura Worl and Steven Buelow**

**Task Description.** Hydrothermal processing provides high destruction and removal efficiencies for a wide variety of organic and hazardous substances. Such substances are aqueous/organic mixtures, pure organic liquids, or contaminated combustible solids (including ion-exchange resins, plastic filters, and cellulosic rags). For all of these substances, hydrothermal processing removes most of the organic and nitrate components (>99.999%) and facilitates collection and separation of the actinides.

A discussion of a general process flow diagram appears in the first quarterly report of this project in FY96.<sup>1</sup>

In general, at temperatures above 500°C, reactions for organic destruction are rapid, and greater than 99% conversion can be achieved in seconds. The reactions are carried out entirely in an enclosed pressure vessel and in dilute concentration so that the reaction heat is absorbed by the water and the temperature can be maintained at any desired level, typically in the 400°C–550°C range.

**Status/Accomplishments.** During the fourth quarter of FY96, Los Alamos National Laboratory researchers continued the study of reactions and the treatment of a wide variety of organic wastes using nonradioactive surrogates. We also installed the

hydrothermal processing equipment in a glovebox.

In order to check the hydrothermal process unit and to train personnel for its operation, we conducted testing using nonradioactive organic mixtures similar to those found in the Los Alamos Plutonium Facility. The following three nonradioactive organic feeds were processed:

- hydraulic oil;
- Dowex 50Wx8™ resin; and
- a mixture of tributyl phosphate (TBP), 1,1,1-trichloroethane (TCE), and vacuum-pump oil (VPO).

The resin mixture consisted of 43.6%resin, 2.0% carboxymethyl cellulose sodium salt (CMC), and 54.4%water by weight. The TBP/TCE/VPO mixture was made up of 5%tributyl phosphate, 5%1,1,1-trichloroethane, 90%vacuum-pump oil, and a trace amount of cerous nitrate.

We performed the experiments at temperatures between 520°C and 540°C and at pressures between 6200pounds per square inch (psi) and 6700 psi. The residence time in the reactor was approximately 2min. We reacted the organic mixtures with 30wt% hydrogen peroxide. The total organic carbon (TOC) concentrations at the inlet of the pressure vessels were 22000ppm for the hydraulic oil,

35000ppm for the resin mix and 35000ppm for the TBP/TCE/VPO mixture. The organic feed flow rates for the different organic feeds were 0.6mL/min, 3.0mL/min, and 1.0mL/min, respectively.

We processed the hydraulic oil and the resin mixture at 520°C and 540°C, and the effluent TOC concentrations were below 10ppm. The TBP/TCE/VPO mixture was processed at 520°C, and the effluent TOC concentration was below 75ppm. The effluent flow was about 20g/min, with pH values of 2.4, 0.7, and 1.5 for hydraulic oil, resin mixture, and TBP/TCE/VPO mixture, respectively. The effluents were acidic because of the presence of sulfuric acid, hydrochloric acid, and/or phosphoric acid caused by reaction of the organic mixtures. In the most corrosive reaction effluent, the concentration of titanium caused by the corrosion of the pressure vessel liner was below 0.2ppm. Assuming uniform titanium-liner corrosion and continuous operation, the titanium concentration in the effluent leads us to predict that the liner will last 42 years.

After completing tests with nonradioactive materials, we disassembled the hydrothermal unit, transported it to TA-55, and installed it in a plutonium glovebox. The process unit is designed to be broken down into small component units that can fit through the window opening of a glovebox. The installation involved more than 20 technical personnel, DOE auditors, and observers. Los Alamos personnel videotaped the installation of the reactor into the

glovebox so that we can review the process. To provide additional operator protection during operation of the hydrothermal unit, we designed, fabricated, and installed a Lexan™ shield enclosure for the reactor and heat-exchanger sections of the process unit. The hydrothermal unit was then pressure-tested and operated with water at room temperature. We did final testing of the unit using 30wt% hydrogen peroxide and operating at 540°C and 6500psi.

We revised the design and operation information for the hydrothermal unit to reflect equipment and operation modifications. The authorization basis was issued for the process, and the readiness assessment (RA) was initiated. This level of review includes DOE participation. We will begin final testing of the unit, using radioactive materials, after the RA is completed.

A conceptual design for the full-scale unit was initiated along with design and testing of slurry pumps. Slurries of cryogenically ground polypropylene filters, paper, plastics, and resins were prepared and tested with various pump and piping configurations. For the various mixtures, we measured the flow rate as a function of pressure, tubing diameters, and slurry viscosity and composition. From experiment results, we developed a preliminary design of the full-scale slurry pump and ordered the necessary components. Assembly and testing of the pump was planned to begin in the first quarter of FY97. Unfortunately all funding for the project was eliminated for FY97.

We issued a final Los Alamos unclassified release in November 1996. In this report we discuss our FY96 progress.<sup>2</sup>

## **References**

1. Steven Buelow, Laura Worl, and D. Kirk Veirs, "Combustibles: Hydrothermal Oxidation," in "94-1 Research and Development Project Lead Laboratory Support Status

Report October 1–December 31, 1995," Los Alamos National Laboratory report LA-13133-SR (May 1996), pp.23-29.

2. Steven Buelow, Laura Worl, and D. Kirk Veirs, "Hydrothermal Processing Unit for Actinide-Contaminated Combustible Wastes—FY96 Final Report," Los Alamos National Laboratory report LA-UR-96-4730 (November 1996).

***Combustibles: Mediated Electrochemical Oxidation***

**Principal Investigator: Wayne Smith**

**Task Description.** Mediated electrochemical oxidation (MEO) destroys the organic component of selected wastes, dissolves the plutonium for later recovery, and leaves the remaining residue matrix in suitable condition for compaction and disposal. The Combustibles Trade Study recently recommended that personnel at Rocky Flats Environmental Technology Site (RFETS) discontinue the current washing baseline and treat their residues either by MEO alone or by MEO in conjunction with another treatment technology. In the latter scenario, plutonium would be removed from Full-Flo™ filters and high-efficiency particulate air filters using MEO, then the filters would be rinsed and dried for repackaging and ultimate disposal at the Waste Isolation Pilot Plant. Other combustible residues would be treated by either catalytic chemical oxidation, by nitric-phosphoric acid digestion, or by an alternate washing process.

**Status/Accomplishments.** RFETS and Los Alamos personnel traveled to Pacific Northwest National Laboratories (PNNL) to evaluate PNNL's capabilities in this area. We learned that they have a pilot-scale MEO unit available for immediate testing and evaluation. PNNL also has a capability to perform tests with radioactive materials on plutonium-contaminated Full-Flo filters obtained from the Hanford Site. These filters

are identical to the ones in use at RFETS; and, because PNNL shares the Hanford site, using these filters would eliminate sending filters from RFETS to another site for testing with radioactive materials. PNNL personnel will participate in a development program aimed specifically at the treatment of the filter media. They are currently preparing a proposal that outlines their development plan and level of participation on the project.

Los Alamos and RFETS personnel had previously visited Lawrence Livermore National Laboratory (LLNL), where extensive work has been done in developing MEO technology. Researchers there also have a pilot-scale apparatus available for future development work. They do not, however, have the capability for testing with radioactive materials. LLNL personnel have sent us a proposal outlining their participation in this project.

In order to meet residue treatment commitments at RFETS, we must give first priority in MEO development to treating filter media. This work can be done more expeditiously at PNNL than at LLNL, because PNNL has a pilot-scale apparatus ready for use, a facility for testing with radioactive materials, and access to plutonium-contaminated residues identical to those in storage at RFETS. A second priority is to develop an MEO-based

treatment process for cellulosic materials, such as paper and cloth rags. This application of MEO technology requires destruction of the organic matrix, which has been shown in previous work to be a very slow process. In order to use MEO as a stand-alone technology for treatment

of RFETS residues, we must find ways to increase the kinetics of this process and to design equipment capable of handling wet cellulosic materials. This is clearly a longer-term development project than filter treatment is. This portion of the project will be conducted concurrently at LLNL.

***Combustibles: Nitric Acid-Phosphoric Acid Oxidation of Contaminated Organics***  
**Principal Investigator: R. A. Pierce, Savannah River Site**

**Task Description.** The purpose of this program is to demonstrate a nitric acid-phosphoric acid destruction technology that can treat a heterogeneous waste by oxidizing the solid and liquid organic compounds and by immobilizing the contaminant metals. The process operates below 200°C and at atmospheric pressure for most materials and at moderate pressures (<20 psig) for complex organics, and the process converts hazardous organics and organic substrates to gases and inorganic salts. Researchers will develop a complete, closed-loop, engineering-scale process that produces little or no organic residue. The process will also isolate hazardous and radioactive metals from solution as an iron phosphate glass or other phosphate-based ceramic. Of particular interest is the use of this process for destroying the combustible residues at Rocky Flats Environmental Technology Site and the <sup>238</sup>Pu-contaminated job control waste at Savannah River Site (SRS).

**Status/Accomplishments.** This wet-chemical process completely oxidizes solid organic waste materials and immobilizes the resulting solution. The process can also be used to remediate other types of organic liquids and ion-exchange resins. The basis for the process stems from extensive studies conducted at SRS. The process uses nitric acid in a

concentrated phosphoric acid medium; nitric acid is the main oxidant for the organic compounds. Phosphoric acid allows nitric acid to be retained in solution at atmospheric pressure well above its normal boiling point.

The process contains three distinct parts: organic oxidation, acid recycle, and metal stabilization. The oxidation step uses nitric acid (HNO<sub>3</sub>) in a concentrated phosphoric acid media as the main oxidant for the organic compounds. The nitric acid products from the oxidation, nitrogen dioxide (NO<sub>2</sub>) and nitric oxide (NO), can be regenerated in an acid recovery system that uses air and water. The net oxidizer for the process would then involve using oxygen from the air added to the acid recovery system. Other oxidation byproducts, such as hydrochloric acid (HCl) (a byproduct of polyvinyl chloride [PVC] oxidation) must be removed from the off-gas stream. The oxidation of the waste to gaseous products leaves all hazardous ions in solution.

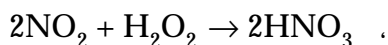
Once oxidation is complete, the phosphoric acid stream becomes the primary feed stream for immobilizing the hazardous ions in an iron phosphate glass. Researchers at SRS have shown that the phosphonic acid stream can be immobilized by adding iron oxide, followed by heating to 1050°C–1150°C.

Progress was made in three areas, with information learned in each area providing data for key FY97 tasks. Progress was made in

- testing the acid recycle system,
- developing an in situ monitoring technique for nitric acid, and
- developing a final form for plutonium-bearing phosphoric acid streams.

### Acid Recycle Testing

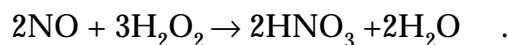
*Discussion.* Because of the likely throughput requirements for the glovebox-scale units, SRS personnel judged that the most appropriate acid recycle approach involves using hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) absorption. Calculations of the maximum theoretical nitric acid concentration expected for absorption of  $\text{NO}_2$  using hydrogen peroxide indicated that high nitric acid concentrations could be obtained by using a solution with 30% hydrogen peroxide. Using the equation



researchers determined that a maximum concentration of 61.3 wt% could be obtained with 30%  $\text{H}_2\text{O}_2$  (approximately 13.3M) and 78.7 wt% with 50%  $\text{H}_2\text{O}_2$  (approximately 18.1M). These calculations do not account for any acid formation that may occur because of  $\text{NO}_2$  absorption by the remaining water in the hydrogen peroxide solution.

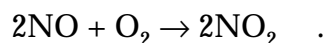
It is important to note that the presence of NO gas in the stream reduces the maximum theoretical

concentration. The reaction of NO with  $\text{H}_2\text{O}_2$  is as follows:



Not only is peroxide-use efficiency reduced, but also a dilution effect occurs from the water in the reaction products. This reaction of NO with  $\text{H}_2\text{O}_2$ , which reduces concentration and adds water, yields theoretical maximum acid concentrations of 47wt% for 30%  $\text{H}_2\text{O}_2$  and 60.8 wt% for 50%  $\text{H}_2\text{O}_2$ .

*Results.* Researchers ran a set of tests in order to look at varying conditions for the acid recycle system. The results from these efforts confirm the importance of converting NO to  $\text{NO}_2$  by introducing air or oxygen ( $\text{O}_2$ ), as



Experimental data show some consistency with the above calculations. When mixing of NO with air occurs with residence times of one minute, high conversion rates are achieved. When residence times are reduced to 30 s, a small reduction in yield occurs. When NO is not converted to  $\text{NO}_2$ , peroxide-use efficiency drops dramatically. The data obtained for 30%  $\text{H}_2\text{O}_2$  are represented in Table 2.

These tests will help optimize the system for use in either a glovebox or a pilot-scale operation. Future work should evaluate 50% hydrogen peroxide instead of 30%, study larger air fractions, and evaluate longer residence times. These changes will produce higher acid concentration for the process and result in smaller secondary waste volumes.

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**Table 2. Experimental Data for 30% H<sub>2</sub>O<sub>2</sub>**

Residence Time (s)	Oxidant for NO	O <sub>2</sub> :NO Ratio	Observed HNO <sub>3</sub> (M)	Theoretical HNO <sub>3</sub> (M)
30	Oxygen	1:2	12.9	13.3
30	Air	1:2	11.3	13.3
60	Air	1:2	12.6	13.3
60	Oxygen	1:2	13.1	13.3
60	Air	2:2	13.3	13.3
60	Not Applicable	0	4.1	9.6

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### In Situ Nitric Acid Monitor

*Discussion.* Direct oxidant monitoring is a capability that has yet to be identified. Currently, only indirect methods exist for determining oxidant concentration in the reaction vessel. Oxidant concentration is important because the addition of too little oxidant will cause the process not to completely destroy the target organics. Conversely, if too much oxidant is added, the oxidant will simply volatilize and be lost to the off-gas system.

The only way to optimize the process is to have a reliable method for readily determining oxidant concentration. While several methods exist, no method has been identified as preferable. SRS researchers view spectrophotometry as the method with the highest probability of success.

*Results.* Proof-in-principle studies have been conducted using simulated process samples. As expected, the ultraviolet-visible absorption band for nitric acid is clearly separated from dissolved iron (the largest light-absorbing metal contaminant). The proof-in-principles result was tested in

nonradioactive solutions, and the data indicate that the development of an in situ probe is possible. If it is determined that the solution is too corrosive for the probe, a sidestream can be separated out and monitored.

SRS personnel have also begun testing in order to identify the type of probe to be used. Initial tests used a spectrophotometer with a 3-mm path length. This probe had the capability of monitoring nitric acid up to approximately 0.4M. This first probe was replaced with a prototype probe using a 1-mm path length that measured up to 0.8M nitric acid. A third generation probe will be designed in FY97 with a 0.1-mm path length. This third-generation probe is expected to measure nitric acid up to 1.5 M. Additional testing will need to be conducted to determine the effects of dissolved organics on light absorption and of elevated temperatures on the probe materials.

### Final Form Testing

*Discussion.* The value of any organic waste treatment process is strongly dependent upon the ability to safely and conveniently place any hazardous



or radioactive metals in a stable, final waste form. The use of a phosphoric acid matrix provides at least two final waste forms, iron/phosphate (Fe/P)-based glass and magnesium/phosphate (Mg/P)-based ceramic. The iron phosphate glass melts at 1050°C–1150°C and has the stability of a high-level waste glass, thereby making it valuable for immobilizing actinide metals. The ceramic is made at ambient temperatures and is stable enough to pass the new Universal Treatment Standards (UTS) for hazardous metals. This stability makes the ceramic valuable for immobilizing Resource Conservation and Recovery Act (RCRA) metals and short-lived radioisotopes such as  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ .

SRS researchers have run tests on  $^{137}\text{Cs}$ -contaminated organics using the iron phosphate glass and have found the glass to be very stable. The leachability for the primary components of the radioactive glass contaminated with  $^{137}\text{Cs}$  were  $\text{P} = 0.031 \text{ g/L}$ ,  $\text{Ba} = 0.002 \text{ g/L}$ ,  $\text{Na} = 3.104 \text{ g/L}$ , and  $\text{Fe} = 0.000 \text{ g/L}$ . Comparing this with the environmental assessment (EA) glass standard for borosilicate glass is difficult because the major components differ. However, both glasses contain comparable amounts of sodium. For comparison, the allowable leachability limit for sodium from the EA glass standard for borosilicate glass is 13 g/L. In addition, toxicity characteristic leaching procedure results indicated that the RCRA metals present did not leach above allowable limits.

*Results.* SRS personnel tested a range of glass formulations by

varying the ferric oxide ( $\text{Fe}_2\text{O}_3$ ) (20 wt %–44wt%), sodium oxide ( $\text{Na}_2\text{O}$ ) (0wt%–7wt%), strontium oxide ( $\text{SrO}$ ) (2 wt %–3 wt %), and phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ) (balance). They also studied a range of cooling times and annealing temperatures. Thus far, it has been found that the  $\text{Fe}_2\text{O}_3$  concentration should be kept in the range of 25%–35% and that the  $\text{Na}_2\text{O}$  concentration should be above 4%. Higher  $\text{Na}_2\text{O}$  can be used if the material tends to devitrify upon cooling. The initial suggested annealing temperature of 450°C was found to be too low. Subsequent testing determined that 500°C was acceptable and that 550°C was too high. The data obtained will be useful in making up the glass formulation for  $^{239}\text{Pu}$  vitrification studies that are to be conducted in FY97.

Comparable tests were conducted at Argonne National Laboratory-East (ANL-E) using the magnesium/phosphate (Mg/P)-based ceramic. In the ANL-E tests, a 20X volume reduction of the residue was assumed to have occurred before the residue is immobilized. Samples of Mg/P ceramic were produced by putting a solution of 48 wt % waste into the ceramic binder. The ceramic is primarily newberyite ( $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ) and has a density of 1.6g/mL.

Leachability tests were conducted, and findings were as presented in Table 3.

In both cases, the experimental results show final waste forms that will meet the necessary storage requirements without using the high temperature

associated with vitrification in a borosilicate glass. Both waste forms

will be considered for plutonium testing in FY97.

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**Table 3. Leachability Tests**

<b>Contaminant</b>	<b>Chromium (ppm)</b>	<b>Nickel (ppm)</b>	<b>Iron (ppm)</b>	<b>Copper (ppm)</b>
Waste Concentration	0.98	112	10.2	35.3
Leached from MgP	<0.01	0.08	0.03	0.03
UTS Limit	0.86	5	Not Applicable (N/A)	N/A

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**General: Modular Systems****Principal Investigators: Richard Hildner and Stanley Zygmunt**

**Task Description.** The objective of this project is to identify tasks within the Rocky Flats Environmental Technology Site (RFETS) residue program in which modular systems may give cost and schedule advantages or in which these systems may reduce uncertainties in the application of the baseline design approach.

**Status/Accomplishments.** During the fourth quarter of FY96, Los Alamos researchers completed the conceptual design of a modular skid-mounted system to unpack, sort, assay, and repack legacy residue drums and cans in Building 707 at RFETS. We conservatively designed the system for batch processing of ruptured packages that contain loose powders and liquids. Drums and cans are processed as wastes. We prepared a basis document, a flow sheet, implementation plans, a preconceptual design of skids, and a floor plan layout. We deferred further planning and documentation because of a reduction in funds late in the year. The draft report is scheduled for distribution the first week in February 1997.<sup>1</sup>

Additionally, we identified an option in which a stand-alone core capability to unpack, sort, assay, and repack

legacy residue drums and cans outside Building 707 would directly support the Residue Elimination Project Rebaselining efforts identified in a Rocky Flats Field Office memorandum.<sup>2</sup> This concept is scheduled for publication in draft form for comments in January 1997.<sup>3</sup>

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3. Richard A. Hildner and Stanley J. Zygmunt, "Build Production Prototype—Modular Treatment System for Stand-Alone Core Capability (SACC) for Residue Unpack, Sort, Assay, Repack—Project Basis Document," Los Alamos National Laboratory report LA-UR-97-522 (January 1997).

### ***Electrolytic Decontamination Transfer System***

**Principal Investigators: Timothy O. Nelson and Douglas E. Wedman**

**Task Description.** Purpose of this task is to electrolytically decontaminate long-term storage inner containers to prepare them for insertion into a second welded container.

**Status/Accomplishments.** Los Alamos National Laboratory Plutonium Facility's (TA-55) configuration management approved the electrolytic decontamination design for the glovebox/fixture assembly.

Los Alamos personnel fabricated the partition wall for the glovebox. The fixture to be placed into the wall design was completed after the final British Nuclear Fuels Limited (BNFL)-type can design was approved by the DOE-EM-66 program manager. We are currently fabricating the fixture to exact BNFL specifications. We completed preliminary tests with nonradioactive materials on a similar fixture, and these tests helped to establish design credibility. Researchers on the Advanced Recovery and Integrated Extraction System (ARIES) project approved a formal design of the process flow.

We chose the proper ultrafiltration module; and we are ordering more of these modules to be used in a variety of tests with radioactive materials, including the can-out project. Tests of a backup filtering system using a centrifuge were successful. Also, we found that the centrifuge can be used as a primary filtration scheme in some specific applications of electrolytic decontamination.

We conducted numerous sodium sulfate electrolyte tests, including using sodium nitrate to decontaminate stainless steel coupons and to decontaminate a glovebox surface. Tests on containers will take place in the first quarter of FY97. Sodium sulfate offers a number of advantages over sodium nitrate, including lower current densities to achieve electropolishing and lower salt concentrations. Decontamination results for the coupons and the glovebox, using sodium sulfate electrolyte, were very satisfactory.

<p><b><i>Surveillance: Digital Radiography</i></b> <b>Principal Investigator: David R. Horrell</b></p>
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**Task Description.** Los Alamos National Laboratory researchers are investigating real-time radiography (RTR) in order to achieve optimum resolution for observing changes in long-term storage containers.

**Status/Accomplishments.** During the fourth quarter of FY96, we characterized the RTR system in Building PF-4 of the Los Alamos National Laboratory Plutonium Facility. We issued a draft analysis of the system and are currently preparing an updated version. Our collaborator at Savannah River Site visited for a week of characterization studies. From this visit and concurrent meetings with Los Alamos investigators, we wrote a brief paper that covers use of the system as-is and a modification and

upgrade path. We performed experiments at the Los Alamos radiographic facility at TA-8, using a zoom lens on the output of the image intensifier. Results were encouraging. We developed a preliminary radiography procedure, which has been approved. In late September we used the preliminary procedure to radiograph the first oxide container produced by the packaging project. We presented an overview of progress at the Materials Identification and Surveillance (MIS) end-of-year review meeting. A staff member is working on the project from Engineering Science and Technology Division. He was trained for unescorted access to PF-4 and is working on becoming a nuclear materials handler in order to facilitate our vault work.

<p><b><i>Surveillance: Tomography</i></b> <b>Principal Investigator: Lynn Foster</b></p>
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**Task Description.** Researchers on this project are investigating the use of computerized tomography (CT) for surveillance of stored nuclear materials. We used computer modeling to develop CT test objects that were representative of items that might be found in stored nuclear materials containers. Two identical test objects were constructed from suitable substitute materials in a joint effort between Los Alamos National Laboratory and Savannah River Site. Each test object contains a module for evaluating the ability of CT to image very dense objects, such as plutonium metal, and modules for evaluating the ability of dual-energy CT to identify material density and composition. We have developed new algorithms for image reconstruction and data analysis that are tailored to solve these density and composition problems.

**Status/Accomplishments.** A round-robin test plan was implemented utilizing both national laboratory and vendor tomography systems at Los Alamos, Livermore, Sandia, and Allied Signal, Inc. The round-robin tests are still in progress at this time. When the tests have been completed, Los Alamos personnel will analyze image data using the advanced reconstruction techniques developed for this project. The capabilities of the different systems will be contrasted with respect to surveillance of stored nuclear materials. We will generate a

final report that contains details of the evaluation and recommendations for procurement of future CT systems to be used for materials surveillance. The projected completion date is December 1996.

We completed the experimental demonstration of the tomographic gamma scanner (TGS). In particular, we studied nondestructive assay of pyrochemical salts using the TGS.

A new algorithm for analysis of pyrochemical salts was developed. The new algorithm specifically addresses the problem of small lumps of plutonium metal that may be present in salts in containers of materials in the vault. When even small lumps are present, traditional gamma-ray assay techniques tend to have very large negative bias in the assay results. The new analysis method assumes that there is a portion of the plutonium in lumps and the remaining fraction is in dilute form throughout the salt matrix. We reported details of the algorithm and results at the 37<sup>th</sup> Annual Institute of Nuclear Materials Management meeting.<sup>1,2</sup>

Using the TGS, we assayed 26 samples that contained plutonium residues; and we used the new lump-correction algorithm to analyze the results. In 6 cases, we detected saturation conditions. When saturation occurs, the assay is insensitive to particle size and the TGS results are invalid. The

corrected assay is compared with the 414-keV assay for each of the remaining cases in Fig. 2. The 414-keV results are biased low by 20% as compared with the reference values determined by calorimetric assay. The corrected values are essentially

unbiased ( $<1\%$ ). However, the 1-std-dev variation of the corrected values averaged over the entire data set was 10%. Most of this variation is expected to be caused by random variations in the counting data.

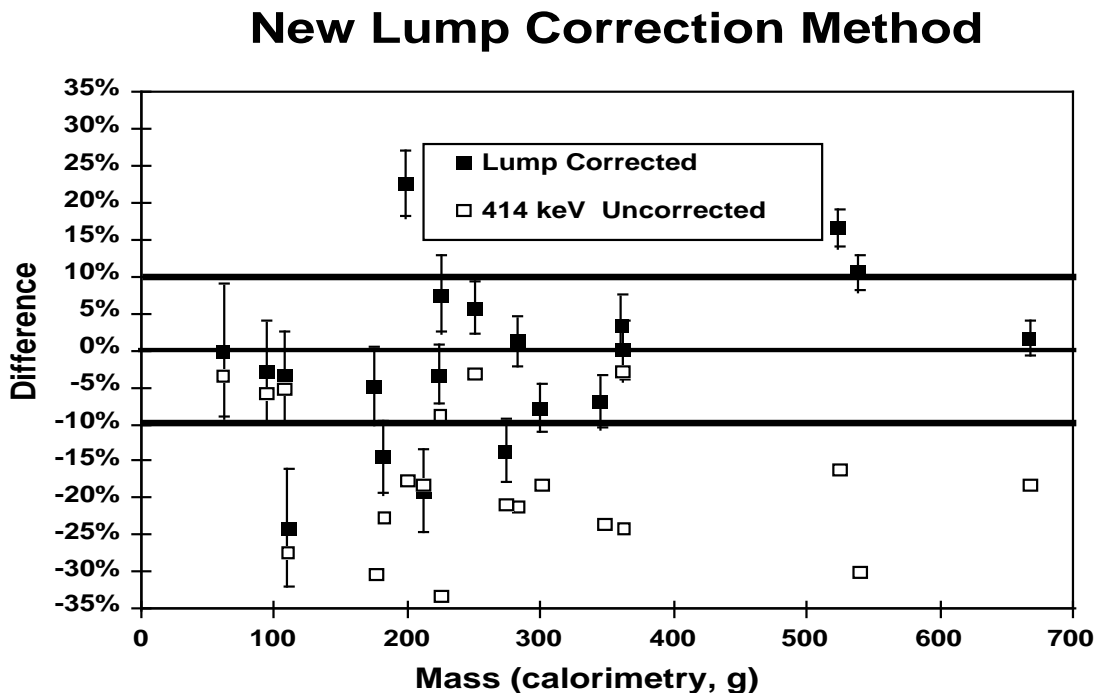


Fig. 2. Results of lump corrections applied to plutonium residues in small cans.

## References

1. T. H. Prettyman, L. A. Foster, and R. J. Estep, "Detection and Measurement of Gamma-Ray Self-Attenuation in Plutonium Residues," 37th Annual Institute of Nuclear Materials Management Meeting, Naples, Florida, July 28–31, 1996, Los Alamos National Laboratory document LA-UR-96-2620.
2. T. H. Prettyman and L. A. Foster, "Transmission Computerized Tomography of Dense Objects," Third Topical Meeting on Industrial Radiation and Radioisotope Measurements and Applications, Raleigh, North Carolina, October 6–9, 1996, Los Alamos National Laboratory report LA-UR-96-1294.

<p><b><i>Surveillance: Pressure-Sensitive Devices</i></b> <b>Principal Investigator: David R. Horrell</b></p>
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**Task Description.** Sandia National Laboratories/New Mexico (SNL/NM) is utilizing miniaturized hydrogen-sensing technology that they developed to be applied toward plutonium surveillance efforts. The sensor technology was developed by SNL/NM, and research is being extended to allow the sensor to operate with high reliability within a plutonium storage vessel. The system also encompasses a power and telemetry system designed to send the sensor signal through a double-walled stainless steel vessel without penetrations.

**Status/Accomplishments.** Progress in the fourth quarter of FY96 was on the

designing the power transformer circuit and mounting this system in a stainless steel container. The coil has been shown to operate successfully through two layers of stainless steel separated by a distance of several millimeters. Power transfer is adequate and 10 bits of data can be transferred several times a minute. Data transfer rate is limited by the charging rate of capacitors in the circuit. The system is currently undergoing gamma-radiation testing at SNL/NM to ensure component durability. Final steps for testing of the prototype will include calibration of the hydrogen sensing system. Delivery of this prototype to Los Alamos is now scheduled for December 1996.



***Surveillance: Pressure-Sensitive Devices*****Principal Investigator: S. E. Nave, Savannah River Site**

**Task Description.** Long-term storage of nuclear materials in hermetically sealed metal containers is an attractive idea. However, such storage has the weakness that the integrity of the container could be compromised by pressurization from the possible evolution of hydrogen. A real-time measure of hydrogen pressure and/or total pressure in the container would give an early warning of any problems and would increase our knowledge about chemical processes that occur in the long-term storage environment.

This project will aid development of fiber-optic sensors for hydrogen detection and/or for total pressure measurement for real-time monitoring of the storage container environment. The sensors will determine hydrogen concentrations from 0.1% to 100% and pressure from 1.5 pounds per square inch (psi) to 36 psi, and the sensors will be based on remote spectroscopic and/or reflectivity measurements by means of fiber-optic cables that enter the storage container through robust hermetically sealed feedthroughs. The use of an all-optical technique results in sensors that are immune to electrical noise and are more corrosion-resistant and radiation-resistant because all construction parts are either glass, ceramic, or simple metal films.

**Status/Accomplishments.** Preliminary design and testing of hermetic metal-sealed, fiber-optic feedthroughs has

been accomplished with development of an epoxy-free feedthrough that will withstand pressure up to 2000 psi at ambient temperature. Personnel at Savannah River Site (SRS) have designed a set of experiments to further test the ruggedness of these fiber-optic feedthroughs. These experiments consist of pressure/leak testing the feedthrough at prescribed time intervals during the process of exposure to water-saturated air at 50°C in order to simulate corrosion by moisture. In a parallel study during the process of irradiation by a cobalt gamma ray source, SRS personnel will simulate accumulated radiation damage in an accelerated fashion.

Work continued increasing the sensitivity of our current thin-film palladium hydrogen sensor. SRS researchers eliminated the film-on-lens geometry and replaced it with a light pipe geometry. So far, SRS researchers have been unsuccessful in getting the chemically produced palladium films to stick to the glass during electrodeless deposition. This lack of success, coupled with the fact that the film needs to be kept thin in order to realize a fast response time for the sensor, led researchers to use sputtering or thermal evaporation in order to coat the substrate. Coating the substrate is difficult to do inside a tube with a diameter less than 1 mm, so a new geometry was required. This geometry consisted of a quartz fiber with the palladium film on its exterior.

A technique has been developed to make a coil shape out of a piece of quartz fiber of any desired length. This technique reduces the sensor volume while maintaining the long path length of the light through the fiber. The light will make many reflections as it travels from one end of the fiber to the other, and the effect from changes in reflectivity of the film will be enhanced. A coating of palladium was sputtered onto the fiber, but too much light was lost at the point where the uncoated ends of the fiber were

epoxied into connectors. Work is underway to overcome this problem by extending the sputter coating to the ends and by overcoating with a low index of refraction organic. This technique looks promising.

SRS personnel registered progress in several areas. An epoxy-free technique was developed for hermetically sealing quartz fibers into stainless tube feedthroughs. This hermetic feedthrough was proof-tested to withstand 2000 psi without leaking.

***Surveillance: Metal, Oxide, Residue Shelf-Life Program***

**Principal Investigator: David R. Horrell**

**Task Description.** In the Metal, Oxide, Residue Shelf-Life Program, we are identifying the materials that will be placed in DOE-STD-3013 containers for storage of at least 50 years and will be made available for Materials Disposition (MD). The DOE sites supporting this project are the Rocky Flats Environmental Technology Site (RFETS), the Babcock & Wilcox Hanford Company (BWHC), and the Savannah River Site (SRS). Their representatives have come together to form the Materials Identification and Surveillance (MIS) working group, which has met several times and will continue to meet regularly.

The working group has identified site materials for evaluation and has completed final draft experimental plans and program. The group also provides an interface between long-term storage and MD issues. The group will consult on sample analysis (chemistry), elevated temperature experiments (calcination), materials monitored in confinement with time (kinetics), thermal profiles for metal and oxide, and development of nondestructive assay (inspection and surveillance of sealed containers). Experimentation data will support the DOE-STD-3013 standard for stabilization and long-term storage.

**Status/Accomplishments.** For this project, Los Alamos personnel will characterize and analyze plutonium-containing remnants of greater than

50 mass % plutonium in order to determine their suitability for storage. Treated and untreated samples are monitored in specially designed storage containers in order to determine material stability, gas generation, gas recombination, reaction rates, and corrosive effects. The primary method of stabilization is thermal heating in air to 950°C, as required by the DOE-STD-3013. Water is considered to have the greatest deleterious storage effect on pure oxide, i.e., from pressure increase. However, impure oxides will present issues for stabilization more complex than simply removing the water.

Nine items of legacy plutonium materials from Hanford Site have arrived at Los Alamos to be evaluated under MIS advisory. All containers were gamma-scanned and the special nuclear material content was determined by calorimetry. Hanford cans have been radiographed and photographed and are ready for analysis. After the MIS advisory meeting, Los Alamos personnel developed gas analysis hardware for Hanford cans. We are now testing this hardware. During the first quarter of FY97, Los Alamos personnel will complete penetration of the first Hanford can. Material from this can will be sent for analysis, and untreated portions of material will be captured in long-term storage for evaluation. By the end of the first

quarter of FY97, we will complete loss-on-ignition (LOI), particle-size, isotopic, elemental, and water-adsorption studies on untreated and treated material. The goal is to start one Hanford can a month through the system. Material will remain under evaluation in surveillance containers in Los Alamos for several years.

Rocky Flats materials are scheduled to be shipped to Los Alamos by April 1997, and the first sample should be in the system for evaluation in May or June 1997. These materials must be evaluated immediately in order to obtain information for the RFETS British Nuclear Fuels, Limited (BNFL) packaging program. SRS materials for MIS are to be shipped in the summer of 1997. The major SRS concern is for mixed metals and oxides that require completion of analysis for thermal stabilization for long-term storage before F-canyon processing is terminated.

To date, Los Alamos and BWHC personnel are establishing a database that includes all the materials destined for DOE-STD-3013 containment at the several sites. Kinetics studies on pure

oxide at elevated temperatures and controlled water conditions are under way at Los Alamos. Also, we have begun x-ray analysis on products from water experiments. With materials from the Los Alamos inventory, we have initiated analysis and stabilization of an impure oxide and a mixed plutonium-uranium oxide. These materials are now awaiting placement in the shelf-life surveillance containers. We have almost completed fabrication of containers for long-term surveillance and kinetics studies, and we are awaiting the delivery of pressure transducers. Limited glovebox or hood space is an identified problem for which we are seeking a solution.

We have scheduled thermal modeling for RFETS and Los Alamos metal and oxide. Preliminary data are available for the metal. Thermal modeling will continue for Los Alamos, RFETS, and DOE complex-wide needs.

Initial studies of supercritical carbon dioxide extraction of water from plutonium oxide are complete. We are investigating the method as an alternative to LOI for impure oxides.

***Surveillance: Raman Spectroscopy***

**Principal Investigator: S. E. Nave, Savannah River Site**

**Task Description.** Long-term storage of nuclear materials in hermetically sealed metal containers is an attractive idea. However, a weakness of such storage is that the state of the stored material cannot be ascertained without opening the container and performing destructive chemical analysis. If the condition of the surface of the stored material could be determined nondestructively by a remote technique, such as fiber-optic Raman spectroscopy, the radioactive risk and exposure to personnel could be greatly reduced. Furthermore, a real-time, in situ determination of the chemical state of the surface of the stored material would give an early warning of any problems and would increase our knowledge about chemical processes that occur in the long-term storage environment. This project will result in the development of a fiber-optic Raman spectroscopy system for real-time, in situ monitoring of the chemical state of the surface of the nuclear storage material.

**Status/Accomplishments.** The new miniature spectrometer and detector for the mobile fiber-optic Raman system have been received and are undergoing testing. Researchers at Savannah River Site (SRS) will achieve greater light throughput with this system than with their current system, because the spectrometer will be better matched to the F/# of the fiber-optic cable. Vendor software that will allow

integrating the detector with the standard SRS data acquisition and analysis software have been received. Researchers are working with the manufacturer.

The final component necessary for the completed system is an excitation laser. SRS still does not have a 670-nm laser, but personnel have repaired one of the 780-nm external cavity lasers that will deliver 500 mW of power. Evidently, this laser was damaged by parasitic oscillations. The oscillations were caused by feedback that in turn was caused by scattering from the sample or from reflecting surfaces in the path between the laser and the sample. The laser manufacturer now recommends an optical isolator between the laser and fiber input, and SRS researchers are waiting for this addition. Personnel have been doing preliminary tests with a low-power laser, but they need the higher-power laser in order to determine the ultimate sensitivity of the system. SRS personnel are also still trying to acquire a 670-nm module to replace the 780-nm module in a second external cavity laser.

Progress was registered in several areas:

- A Raman probe constructed only of metal and glass components (no epoxy) has been assembled and tested. This probe was shown to give a low background signal that

will allow observation of Raman peaks near the laser line with excellent signal-to-noise ratio.

- The major components of a mobile fiber-optic Raman system have been acquired and assembled for operation at 488 nm, 514 nm, and 780 nm.

- Integration of the manufacturer's software drivers for the charge-coupled device detector into the SRS data acquisition and chemometric data analysis package is almost completed.

### ***Surveillance: Acoustic Resonance Spectroscopy***

**Principal Investigators: D. Kirk Veirs and Clinton Heiple**

**Task Description.** Los Alamos personnel are developing acoustic resonance spectroscopy (ARS) as a noninvasive method for determining the gas composition and pressure buildup in metal, oxide, and residue storage containers. Gas resonances are easily detected inside an otherwise empty container. The amplitude of the gas resonances varies with gas pressure; and the frequency varies with gas composition, as predicted by acoustic resonance theory.

**Status/Accomplishments.** Los Alamos investigators have calculated the sensitivity of ARS to detect changes in gas composition, based on shifts in the frequency of the gas peak by 1 Hz. These calculations have been done for mixtures of helium, hydrogen, and argon. Although helium and hydrogen are similar in mass, the frequency shift when hydrogen is mixed with helium is nevertheless easily detectable. From our calculations we can predict that an increase of less than 0.5 torr hydrogen in a local atmosphere of helium (590 torr) would be detectable. Our report summarizes a set of experiments designed to evaluate the feasibility of using ARS to measure gas pressure and gas composition inside the proposed container.<sup>1</sup>

In a simulation of double-containment geometry, we have demonstrated that gas resonances can be created and observed in the simulated inner can with transducers mounted on the outside of the outer can. We used mechanical coupling between the two containers. Several coupling geometries were tested, including stainless steel cylinders, 45° stainless steel cones, and a stainless steel thin-walled ring. The cylinders were most effective. Epoxying the cylinders in place produced the best signal.

Interaction between gas and shell resonances is a substantial problem in signal analysis. As the driving frequency approaches a shell resonance, the amplitude of shell-wall motion increases. If this motion can be coupled to gas motion, then the gas will be driven harder, leading to a larger gas peak signal. Transferring energy to the gas extracts energy from shell motion and reduces shell motion amplitude. We tested this physical model numerically by calculating the signal amplitude and the frequency that results from the sum of two damped, driven harmonic oscillators interacting as described. The similarity between calculated results and experimental observation suggests that the physical model of the interaction is substantially correct.

In the fourth quarter of FY96, we investigated the relation between linewidth and line positions. The equations for calculating line positions and linewidths contain the same molecular parameters, and these observables may change to provide identical information. In order to test the proposition that linewidths and line positions of acoustic gas modes are related, we conducted experiments using mixtures of gases in a spherical resonator. The spherical resonator geometry minimizes gas resonance linewidths and was chosen to

emphasize the fundamental relations. We calculated compositions in which the resonate frequency of a number of gas mixtures was the same. We achieved gas composition by using a pressure gauge with a resolution of 1 pound per square inch (psi); this low resolution is shown by the fact that the resonate peaks for each pair do not occur in the same position. In the following graphs, the frequencies were shifted so that the peaks overlapped. For gas mixtures involving only inert gases, the observed resonances have identical linewidths (Fig. 3).

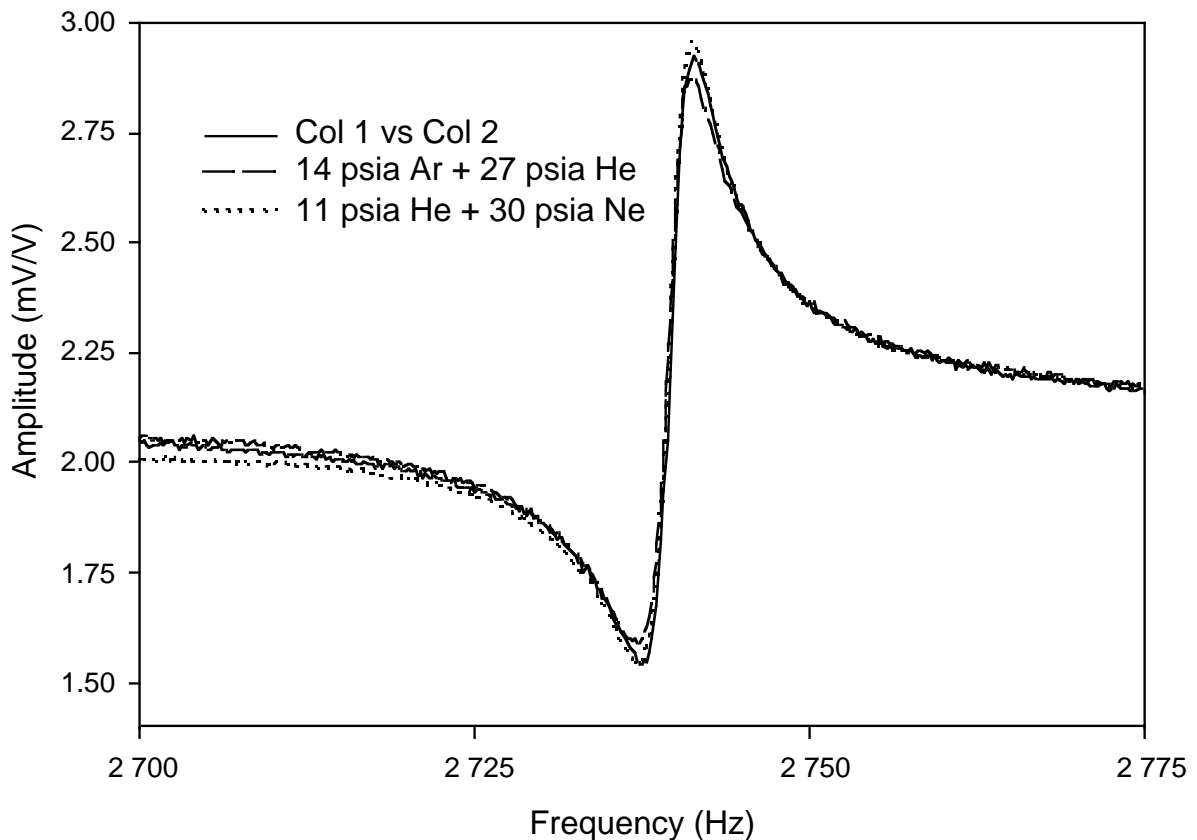


Fig. 3. Observed line shapes for inert gas mixtures in a spherical resonator.



Gas mixtures containing nitrogen and carbon dioxide, as well as monotomic, inert gases, were examined. The gas compositions were chosen so that the acoustic response of each mixture would be at the same frequency, as shown in Fig. 4. The gas compositions appear in Table 4. It is clear that the data are quite similar, yet linewidths

seem to decrease for resonances that contain nitrogen and carbon dioxide. In order to be confident in this effect, the spectra need to be fit using an appropriate theory. If the changes in the linewidths are due to energy loss at the surfaces, then this effect may be magnified using a geometry with greater surface-to-volume ratio, such as a cylindrical cavity.

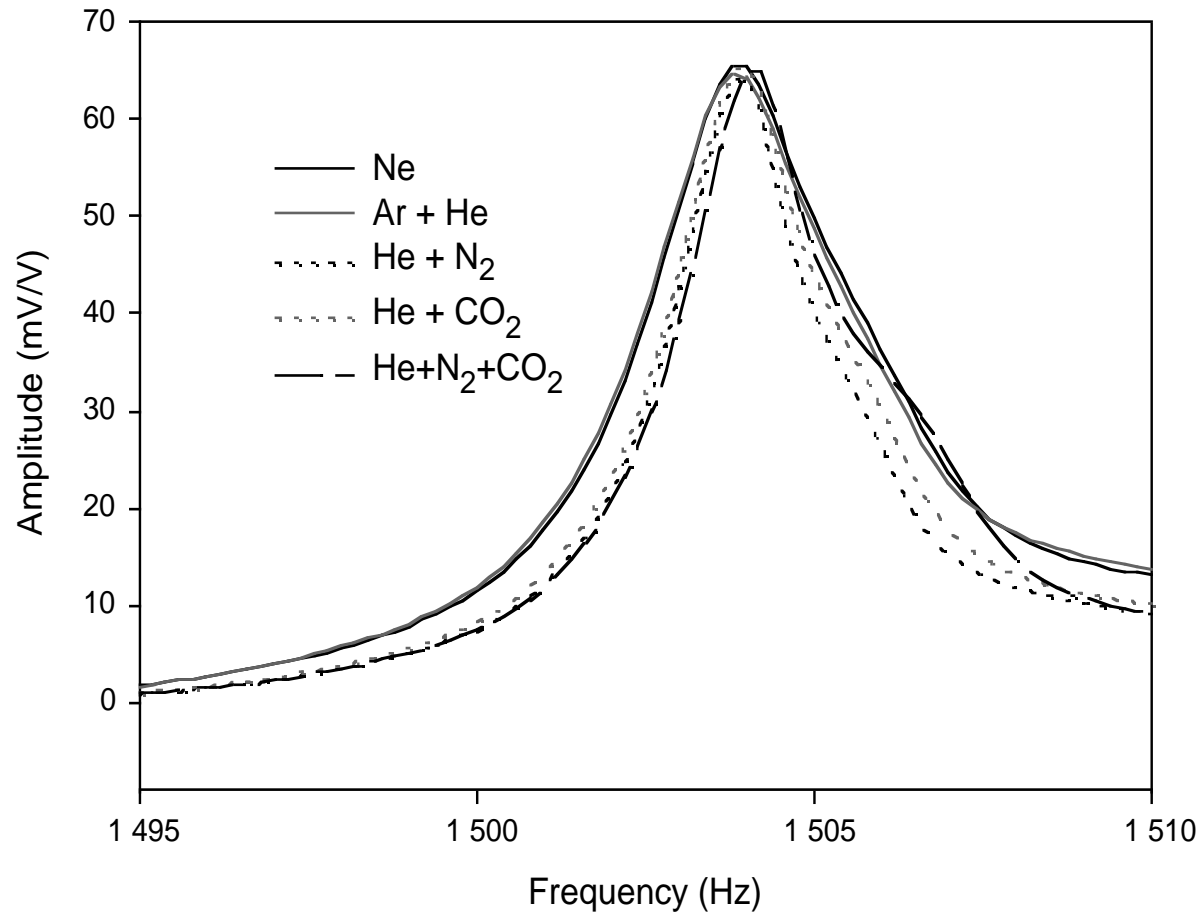


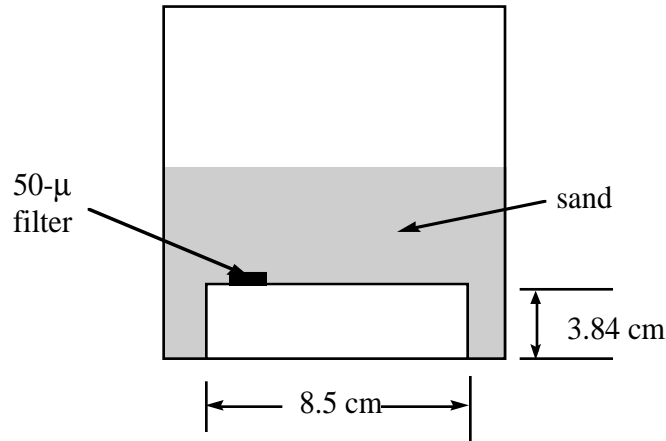
Fig. 4. Observed line shapes for inert mixtures in a spherical resonator.

**Table 4. Gas Pressures in psi for Five Compositions that Yield the Same Speed of Sound in the Gas**

	He	Ne	Ar	N <sub>2</sub>	CO <sub>2</sub>
Mixture 1	0.0	41.0	0.0	0.0	0.0
Mixture 2	22.55	0.0	18.45	0.0	0.0
Mixture 3	17.2	0.0	0.0	23.8	0.0
Mixture 4	27.1	0.0	0.0	0.0	13.9
Mixture 5	23.5	0.0	0.0	8.8	8.8

We inserted the pipe section into the storage can, glued one end of the pipe to the storage can bottom, and then glued a circular plate on the top end of the pipe as a lid. The circular plate had a 50- $\mu$  filter glued onto a small hole in

order to let gas pass into the cavity while keeping out the material in the can. The cavity was covered with sand in order to mimic the effect of plutonium dioxide powder on the cavity. The design of this advanced cylindrical cavity is presented in Fig. 5.



**Fig. 5. Design of advanced cylindrical cavity.**

The sand effectively dampens all modes associated with the container except those associated with the portion of the can bottom that is protected by the cavity. We glued

transducers to the bottom and acquired spectra. Figure 6 shows the spectrum of this arrangement when the interior of the can is filled with 40 pounds per square inch, absolute

(psia) argon. We observed a number of small gas peaks. The frequencies of these gas peaks were calculated using

$$v = \frac{c}{2} \sqrt{\left(\frac{n_z}{l}\right)^2 + \left(\frac{\alpha_{n,m}}{a}\right)^2},$$

where  $l$  is the height of the cylinder;  $a$

is the radius;  $c$  is the velocity of sound of the gas;  $n_z$  is the index for the longitudinal waves and takes on the values of 0, 1, 2, 3...; and  $\alpha_{n,m}$  are the values of  $x$  where the derivative of the integer Bessel function is zero.<sup>2</sup> The calculations were done in MathCad™ and used the speed of sound in argon at 298K(31997cm/s).

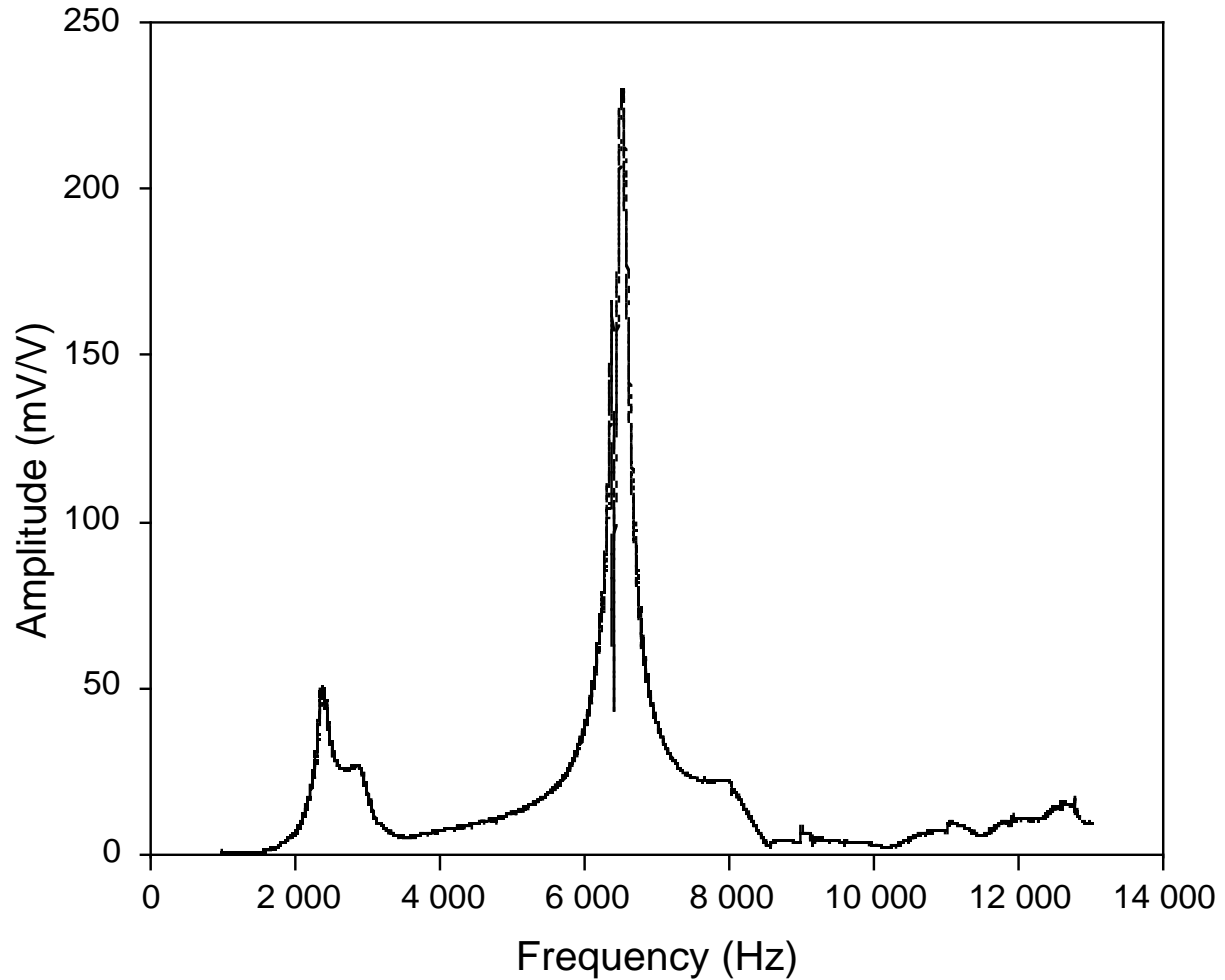


Fig. 6. Acoustic spectrum of a 1.5-in.-high cylindrical cavity covered with sand as shown in Fig. 5. All observed gas resonances are predicted by the cited equation. The sand damps out most of the container resonances in this frequency range. All the broad features are container resonances associated with the undamped drumhead motions on the bottom surface where the transducers are attached.

Gas peaks observed from 1000 Hz to 13 000 Hz were compared with the calculated resonances. All observed

gas peaks were predicted by the preceding equation, as shown in Table 5.

**Table 5. Gas Resonances Predicted by the Equation and Observed Resonance Intensity**

$n_z$	$m$	$n$	Frequency	Observed Intensity
0	0	0	0.0	
0	1	0	2 206.0	5 mV
0	2	0	3 660.0	1 mV
1	0	0	4 196.0	1 mV
0	0	1	4 591.0	-----
1	1	0	4 741.0	2.5 mV
0	3	0	5 034.0	-----
1	2	0	5 568.0	1 mV
1	0	1	6 220.0	3 mV
0	4	0	6 372.0	120 mV?
0	1	1	6 388.0	120 mV?
1	3	0	6 554.0	-----
1	4	0	7 629.0	1 mV?
1	1	1	7 643.0	1 mV?
0	5	0	7 687.0	2 mV
0	2	1	8 035.0	10 mV
2	0	0	8 393.0	1 mV
0	0	2	8 406.0	-----
2	1	0	8 678.0	1 mV
1	5	0	8 758.0	-----
0	6	0	8 988.0	-----
1	2	1	9 065.0	1 mV
2	2	0	9 156.0	7 mV
1	0	2	9 395.0	2 mV
2	0	1	9 566.0	2.5 mV
0	3	1	9 604.0	0.1 mV
2	3	0	9 787.0	0.5 mV
1	6	0	9 919.0	0.1 mV
0	1	2	10 220.0	0.2 mV
0	7	0	10 280.0	-----
1	3	1	10 480.0	1 mV
2	4	0	10 540.0	0.5 mV?
2	1	1	10 550.0	0.5 mV?
1	1	2	11 040.0	2 mV
1	7	0	11 100.0	0.5 mV
0	4	1	11 120.0	1 mV
2	5	0	11 380.0	-----
0	8	0	11 560.0	-----
2	2	1	11 620.0	0.5 mV
2	0	2	11 880.0	6 mV
1	4	1	11 890.0	1 mV
0	2	2	11 950.0	4 mV
0	0	3	12 190.0	1 mV
2	6	0	12 300.0	-----
1	8	0	12 300.0	-----
3	0	0	12 590.0	4 mV
0	5	1	12 610.0	0.1 mV
1	2	2	12 660.0	0.5 mV
2	3	1	12 750.0	1 mV
3	1	0	12 780.0	6 mV
1	0	3	12 890.0	0.5 mV

There were no extra peaks. We did not observe some predicted resonances. These resonances generally had no longitudinal component and were composed of higher orders of the radial modes. Since the transducers were located on the bottom, they would most effectively excite and detect longitudinal modes. The radial modes have structure as a function of the radius, and it would be interesting to see whether the modes that were not observed had nodes in the pressure where the transducers were located. The agreement between observed gas peaks and predicted gas peaks is nothing short of astounding, considering the crudeness of the arrangement.

It may be useful to quantitatively examine this data. The data can be fit using the theoretical approaches outlined in the previously mentioned report by Veirs, Heiple, and Baiardo. Quantitative values for the resonant frequencies can be compared with the predicted frequencies. The equation cited previously has three parameters with some uncertainty  $c$ ,  $l$ , and  $a$ . These can be fit using the equation and the observed frequencies. This

procedure will yield some indication of the accuracy of the calculated resonances. The linewidths obtained and their errors would also be of interest. The effect of the can resonances on the gas modes can be quite large as seen in the resonance at 6380 Hz. Does this resonance shift or broaden because of the can resonance? Because the signal is so large, it would be useful for monitoring inside doubly sealed containers if the line position, linewidth, and intensity parameters could be related to unperturbed values.

## References

1. D. Kirk Veirs, Clinton Heiple, and Joseph Baiardo, "Feasibility Study of Measuring Gas Composition and Pressure inside a Sealed Plutonium Residue Container with Acoustic Resonance Spectroscopy," Los Alamos National Laboratory report LA-13058-MS (in press).
2. Philip M. Morse, *Vibration and Sound* (McGraw-Hill Book Company, Inc., New York, 1948), pp. 398-399.

***Core Technology: Actinide Solution Chemistry***

**Principal Investigator: John M. Berg**

**Task Description.** In this work, Los Alamos National Laboratory personnel seek to describe aspects of the solution chemistry of actinide elements in legacy residues and in proposed residue treatment processes. We hope to describe these aspects well enough to guide decisions about stabilization and disposition and to enable efficient optimization of treatment processes.

Plutonium residue stabilization and treatment processes need to be efficient and to produce a stable product economically. Aqueous chemical separations will be required for primary treatment and post-treatment following stabilization of many residues. Our work will seek to measure critical thermodynamic parameters governing actinide chemistry so that treatment and separation processes can be designed and optimized quickly.

**Status/Accomplishments.** Sample preparation, data acquisition, and data analysis activities on both the Pu(IV) nitrate acid system and the Pu(VI) chloride near-neutral system all progressed substantially during the fourth quarter of FY96. Los Alamos National Laboratory Chemical Science and Technology Division participants prepared ~ 0.5 g of plutonyl monocarbonate ( $\text{PuO}_2\text{CO}_3$ ) for characterization as a pure starting material for Pu(VI) solution speciation

studies. We collected extended x-ray absorption fine structure (EXAFS) spectra of  $\text{PuO}_2\text{CO}_3$  and compared them with a model calculation, using idealized rutherfordine analog structure. Our conclusion at this point is that there are some structural differences between the two systems. We also obtained powder x-ray diffraction (XRD) of two plutonium solids from solubility studies. One solid is believed to be  $\text{PuO}_2\text{CO}_3$  and matches the XRD of the rutherfordine structure extremely well. The other solid is similar to rutherfordine, but has different intensity ratios. Its structure has not yet been assigned. We have also collected EXAFS spectra and near-infrared electronic spectra of a series of solutions containing Pu(VI) chloro complexes and are proceeding with the data analysis.

Nuclear Materials Technology Division participants prepared and collected electronic absorption spectra in the visible and near-infrared regions of more than 500 additional solution samples. The samples contain Pu(IV) and nitrate under a range of conditions that include the stability regions of seven different Pu(IV) nitrate complexes. This completed the data-acquisition phase on this chemical system. We are currently analyzing those data to obtain thermodynamic constants for complexes at 10 ionic strengths.

Concurrently, we have begun experiments to investigate the effects other dissolved salts have on the nitrate system. We have acquired initial spectroscopic data on

the effects of  $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$  and  $\text{Cl}^{-}$  on the formation of  $\text{Pu}(\text{NO}_3)_n^{4-n}$  complexes. The experimental phase of this work will continue through the third quarter of FY97. Data analysis will proceed concurrently.

**Core Technology: Actinide Solution Chemistry**

**Principal Investigator: D. G. Karraker, Savannah River Site**

**Task Description.** An attractive process for the destruction of glovebox waste involves oxidation by nitric acid in a concentrated phosphoric acid solution. After the oxidation of organic matter, plutonium and other metal ions will accumulate in the phosphoric acid. This study of the chemistry of plutonium in concentrated phosphoric acid is aimed at determining the properties of plutonium phosphate solutions and investigating methods for recovering plutonium and recycling  $\text{H}_3\text{PO}_4$ .

**Status/Accomplishments.** Plutonium phosphate solutions were prepared from plutonium purified by anion exchange and precipitated as Pu(IV) oxalate. Plutonium oxalate was dissolved in hot 85% (14.6 M)  $\text{H}_3\text{PO}_4$ . The viscous solution would not filter by vacuum with a medium frit (10–50  $\mu$ ) filter and syringe filters dissolved in the  $\text{H}_3\text{PO}_4$  solution. After solids had settled, the solution was assayed by alpha counting as 170g/L. The density of the solution was measured as 2.80g/mL; the density of 85% $\text{H}_3\text{PO}_4$  is 1.689g/mL.

The absorption spectra of dilutions of this pink solution, measured with a Hewlett-Packard diode array spectrophotometer, identified the Pu(IV) valence. The spectra of seven dilutions established a standard curve of absorbance as compared with the concentration to be used for measuring plutonium concentration.

The pink Pu(IV) phosphate solutions were reduced to blue Pu(III) both by zinc dust and ferrous sulfamate; dilutions of the blue  $\text{PuPO}_4$  solution were used to measure a standard curve of absorbance as compared with Pu(III) concentration in 85% $\text{H}_3\text{PO}_4$ . The blue solutions slowly oxidized over 1–3 days to Pu(IV). Attempts to oxidize Pu(IV) solution to Pu(VI) with  $\text{KMnO}_4$  were unsuccessful.

Bjorklund<sup>1</sup> reports precipitation of a mixed oxalate-phosphate from phosphoric acid. This method was attempted on plutonium solutions that ranged from approximately 1mg/mL to 17mg/mL. The experiment was successful only when an equal volume of 0.9M oxalic acid was mixed with the 17mg/mL solution. Tenfold dilution of 17mg/mL Pu(IV) solution precipitated Pu(IV) phosphate as a gelatinous solid that did not appear useful for plutonium separation.

On the presumption that Pu(III) phosphate might be less soluble than Pu(IV) phosphate, researchers reduced 170mg/mL Pu(IV) phosphate to Pu(III); but no precipitate formed. The solubility of  $\text{PuPO}_4$  is evidently too high for a plutonium recovery process.

The current objective of this work is to find a feasible method for separating plutonium from the concentrated  $\text{H}_3\text{PO}_4$ . Both Pu(IV) and Pu(III) phosphates are very poorly



soluble in dilute acid,<sup>2,3</sup> but their solubility increases greatly as  $\text{H}_3\text{PO}_4$  becomes more concentrated. It is apparent that the solubility of plutonium phosphates in concentrated  $\text{H}_3\text{PO}_4$  will not limit the capacity of the process. One proposed objective of this study, the determination of the solubility of plutonium in 85%  $\text{H}_3\text{PO}_4$  at various temperatures, appears experimentally very difficult and has been postponed in favor of determining a method for plutonium recovery from  $\text{H}_3\text{PO}_4$ .

A single attempt to vacuum-distill 85%  $\text{H}_3\text{PO}_4$  at pot temperatures up to  $150^\circ\text{C}$  succeeded only in producing 96%  $\text{H}_3\text{PO}_4$  in the pot ( $d=1.722\text{g/mL}$ ) and water in the distillate ( $d = 0.998$ , neutral to litmus). Equipment was ordered to permit higher pot temperatures.

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***Core Technology: Chemical and Physical Interactions of Actinides with Surfaces***  
**Principal Investigator: David Morris**

**Task Description.** Researchers on this project are focusing on molecular spectroscopic characterization of the interaction of plutonium and other actinides with several classes of important residues, including combustibles (ion-exchange resins and cellulosic materials) and incinerator ash.

**Status/Accomplishments.** Los Alamos National Laboratory personnel continue to make significant progress on two research fronts in this project: characterization of the influence of concentrated nitric acid on anion-exchange resins and characterization of the interaction of uranyl nitrate complexes with anion-exchange resins. In addition, we began studies during this reporting period on the interaction of uranyl species with a pure cellulosic material. Details of these efforts are provided in this report.

We have made a postdoctoral fellowship offer for work on microscopic x-ray fluorescence and vibrational spectroscopic imaging, with a projected starting date of January 1997 for the new person.

We have completed the initial suite of experiments to characterize the nature and extent of the interaction of uranyl nitrate solution species with the anion-exchange sites on Dowex-11<sup>TM</sup>, a typical strong anion-exchange material. We examined these

interactions as a function of loading capacity on the resin, nitric acid concentration in the feedstock, and extent of drying/rehydration of the loaded resin.

Most investigations were done using time-resolved luminescence spectroscopy, but some work was also done on the feedstock solutions using UV/visible absorption spectrophotometry. The absorption spectra for the uranyl species obtained as a function of nitric acid concentration clearly show that the spectra change in response to increasing degrees of complexation of uranyl by the nitrate anion. An example of the luminescence behavior of the uranyl nitrate/resin system is shown in Fig. 7.

The native resin (i.e., no uranyl loading) has a weak luminescence signal. As the anionic uranyl species are exchanged into the anion sites of the resin, the resin signal becomes quenched and the signal from the uranyl species begins to dominate. This phenomenon suggests the existence of some significant degree of electronic coupling between the uranyl nitrate species and the resin chromophore (most likely the styrene ring system). Similar behavior was noted in all nitric acid concentrations. Existing data comparing the time-resolved spectral signatures from the uranyl nitrate-loaded resins suggest that one uranyl

nitrate species-resin site pair in these systems dominates, rather than do multiple uranyl species or multiple

resin sites. Future work will focus on other resin materials (e.g., Reillex™) and plutonium nitrate species.

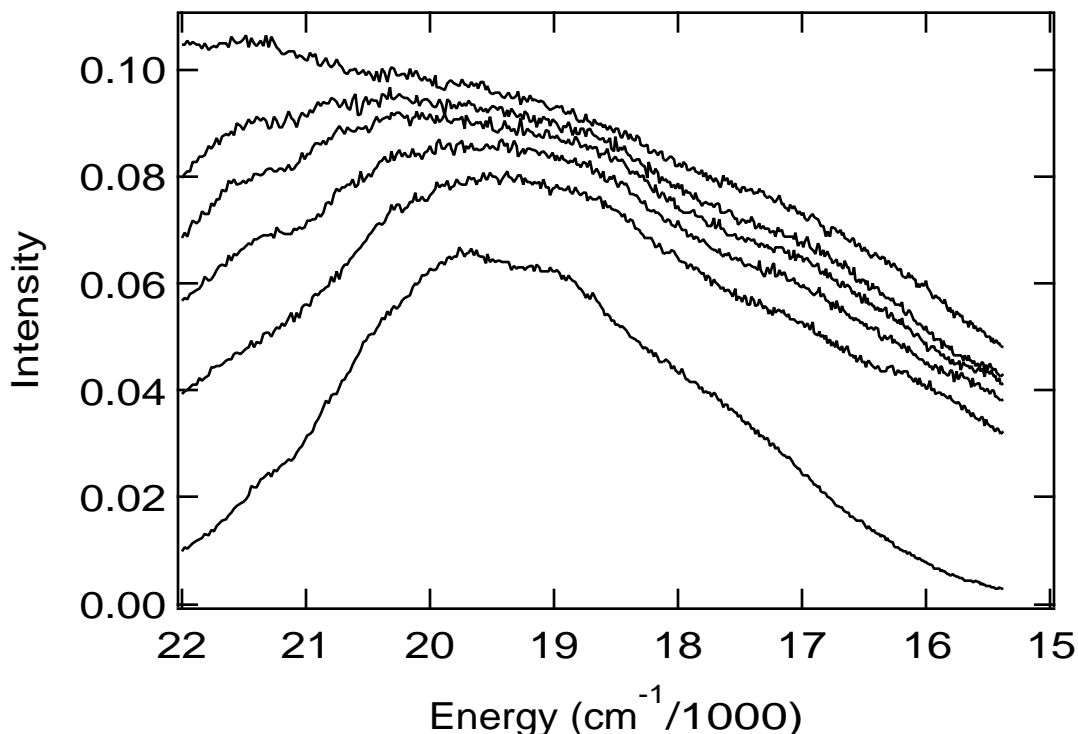


Fig. 7. Luminescence behavior of the uranyl nitrate-resin system in 8 M nitric acid. Curves are as follows, from top to bottom: 0% loading, 10% loading, 25% loading, 50% loading, 100% loading, and 8 M nitric acid without resin.

Also, we began initial studies on the interaction of uranyl species with a pure cellulosic material. The material chosen, Whatman CF1™, is a long-fibered, high-surface-area cellulose that represents a surrogate for processing wastes (such as paper towels and laboratory clothing) that make up a significant fraction of the combustible plutonium residue inventory in the DOE complex. The aliphatic alcohol side chain is oxidized to a carboxylic acid to some extent in this material, providing an excellent source for binding of actinide cations.

Our experiments have focused on varying uranyl solution concentrations and solution pH values in order to look for variations in the interactions between uranyl and the cellulose substrate. Thus far, we have observed unusual pH fluctuations in the reactions between uranyl and the cellulose. These reactions suggest that the mode(s) of interaction is not simple physisorption. The luminescence spectral data suggest that either little uranium is actually sorbed to the material and/or that the sorption reaction leads to quenching

the uranyl luminescence, for example, from redox changes in the uranium and the substrate.

We have also made significant progress in characterization of the influence of high nitric acid concentrations and aging on process ion-exchange resins. This characterization is important for a number of reasons. First, the aging of the resin chemical and physical structure is quite likely to alter the manner and degree to which plutonium is bound to the material. Second, potentially unstable (explosive) forms of the resin may be generated after extended exposure to the high concentrations of nitric acid that are used in the separation process.

As noted in previous progress reports, the instrumentation required to examine actual plutonium-contaminated waste resins by optical spectroscopic methods is currently being assembled in the Los Alamos National Laboratory Chemistry and Metallurgy Research Building. In the meantime, however, we have undertaken a series of experiments designed to detect any changes in the molecular structure of the resins as a function of extended exposure to a graded series of nitric acid concentrations. Thus, we have prepared a series of Dowex-11 samples in 4 M, 8 M, and 12M HNO<sub>3</sub>. A control sample, used as received with chloride ions at the exchange sites, was prepared in deionized water. To accelerate any effects, we stored these samples in an oven at 50°C. A variety of changes occurred in

the Raman vibrational spectrum of Dowex-11 that was aged under these conditions.

Figure 8 displays the low-wave-number ( $\sim 550\text{--}1100\text{ cm}^{-1}$ ) Raman shift window for the artificially aged and control samples of Dowex-11. The samples stored in nitric acid clearly demonstrate uptake of the nitrate ion as observed by the appearance of the symmetric N-O stretching band around  $1050\text{ cm}^{-1}$ . All of the Raman peaks become progressively weaker as the acid concentration is increased, probably because of self-absorption effects associated with the graded darkening of the resin upon uptake of the nitrate anion. In the lower-wave-number window, the acid-concentration-dependent changes observed for the vibrational bands are characterized by graded depletion of two clearly observed bands at  $623\text{ cm}^{-1}$  and  $1005\text{ cm}^{-1}$ .

The identification of these bands is of primary importance for understanding their association with the binding of nitric acid. On one hand, these bands may simply be associated with the binding site, and their graded depletion is indicative of the extent of binding of nitrate ions. However, it is possible that these bands are associated with chemical structures in the resin that are susceptible to breakdown by exposure to nitric acid. To test this idea, we are manipulating a small portion of the resin samples in an effort to completely exchange the nitrate ions, thereafter examining the spectra for the extent of recovery of these bands.

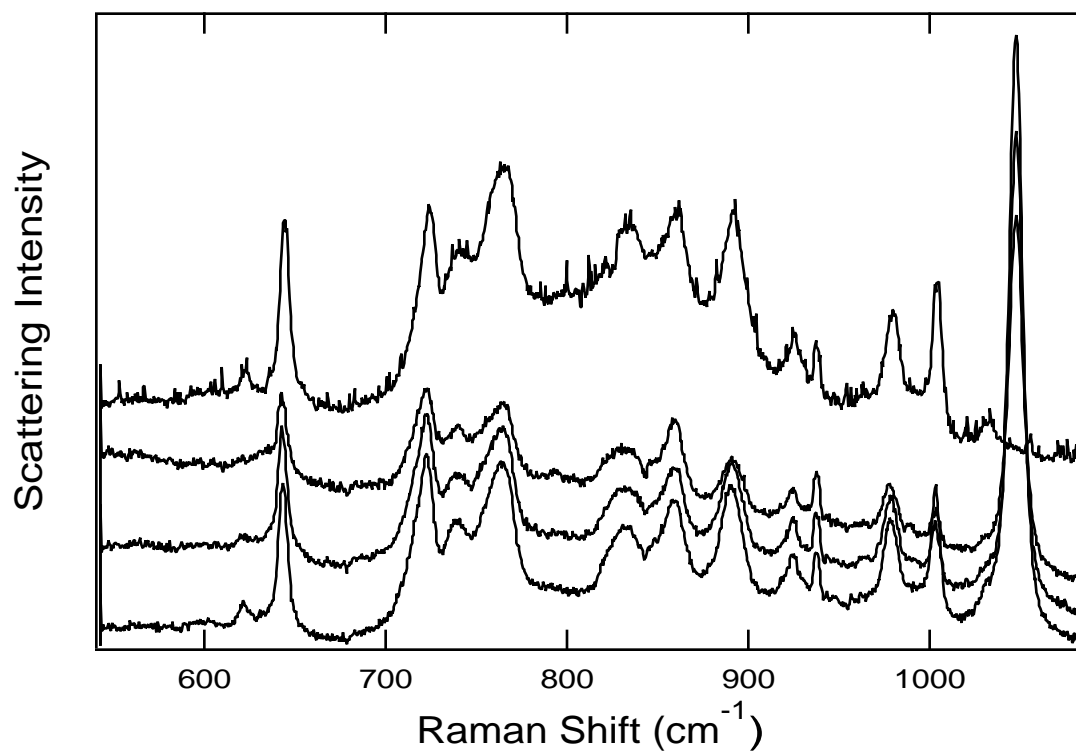


Fig. 8. Low-wave-number Raman shift window for the artificially aged (4 weeks at 50°C) and control sample of Dowex-11. Curves are as follows, from top to bottom: control sample, 12-M nitric acid sample, 8-M nitric acid sample, and 4-Mnitric acid sample.

***Core Technology: Changes in the Chemical State of Plutonium***

**Principal Investigators: D. Kirk Veirs and Mary Neu**

**Task Description.** The purpose of this work is to identify and characterize changes in the physiochemical state of the myriad plutonium compounds found in residues.

**Status/Accomplishments.** Four oxidation states (III, IV, V, and VI) of plutonium may coexist under particular conditions. An efficient method of determining the states actually present in various matrices would promote an ability to model and predict the fate of plutonium in process streams and in other environments.

As a first step toward using x-ray absorption near-edge structure (XANES) to determine the oxidation state of plutonium in complex matrices, Los Alamos National Laboratory researchers measured the edge energies of plutonium aquo ions. The  $L_3$  XANES spectra of plutonium are primarily determined by the valence state and the presence or absence of the trans dioxo moiety. We observed a progressive shift to higher energy with increasing valence according to the equation:

$$\text{edge energy (eV)} = 18\,054 + 1.68^* (\text{oxidation state})$$

In addition, we observed that the general spectral shape of the (III) and (IV) species spectra is clearly different

from the dioxo-containing (V) and (VI) species spectra, with the first maximum much larger and sharper for the (III) and (IV) spectra than for the (V) and (VI) spectra.

Chemical speciation, as the determinant of reactivity of plutonium, is critical toward understanding and predicting chemical and physical behavior under process and storage conditions. The number of accessible oxidation states for plutonium in aqueous solution (Four oxidation states [III, IV, V, and VI] may coexist under particular solution conditions.)<sup>1</sup> adds to the chemical complexity of the plutonium.

XANES is a technique that may be used to determine the oxidation state and the local chemical environment of elements, even at relatively low concentrations and without requiring extensive sample preparation that could induce artifacts.<sup>2</sup> Establishing edge energies and near-edge features of known plutonium aquo species for the different oxidation states is the first step in determining which oxidation states are predominant in complex matrices, for example, at the solution/surface interface or in amorphous solids.<sup>3</sup> While XANES spectra for uranium and the complete suite of neptunium oxidation states have been reported,<sup>4,5</sup> no systematic studies have been performed for plutonium.

Actinide solutions that contain a single oxidation state have been prepared electrochemically<sup>1</sup> and have been verified (both before and after XANES analysis) with ultraviolet-visible absorption spectrum-near infrared (UV-VIS-NIR) absorption spectroscopy. Each sample contained more than 98% of a single plutonium species. Similar chemical environments around each of the plutonium cations were produced by preparing and studying the aquo species. We prepared  $\text{Pu}^{3+}$ ,  $\text{Pu}^{4+}$ , and  $\text{PuO}_2^{2+}$  in 1 M  $\text{HClO}_4$ ; and we prepared  $\text{PuO}_2^+$  in perchlorate at pH 3 and subsequently stabilized it for disproportionation by adjusting the pH of the solution to 6. Plutonium L-edge x-ray absorption fine structure (XAFS) spectra

- were measured in the transmission (III, IV, VI) or fluorescence (V) mode;
- were calibrated by defining the first inflection point of the K-edge spectrum of a zirconium foil as 17999.35 eV; and
- were normalized by setting the value of a polynomial fit through the pre-edge region to zero and the value of a polynomial fit through the extended x-ray absorption fine-structure (EXAFS) region to unity at 18 075 eV (defined as the ionization threshold).

The energies of the edges were determined in two ways: (1) as the inflection point of the edge and

(2) as the energy of the arc tangent in least-squares fits of the arc tangent plus Gaussians of the XANES region.<sup>6</sup>

When valence increased, we observed significant shifts to higher energy. In addition, the general spectral shape of the (III) and (IV) species is clearly different from the dioxo-containing (V) and (VI) species (Fig. 9). Specifically, the first maximum is much larger and sharper for the (III) and (IV) spectra, whereas the (V) and (VI) spectra exhibit a prominent shoulder on the high-energy side of this peak. The energies of the edge and “white line” positions are listed in Table 6.

When the edge shifts are measured by the second derivatives, they generally increase as the formal oxidation state of the absorbing metal atom increases so that (III), (IV/V), and (VI) are easily distinguished. We noted that while the overall shapes of the (IV) and (V) states allow unambiguous assignment, their energies are quite similar. If the trend in position reflects the charge, this circumstance might be explained by the increase in covalency (and diminution of actual difference in charge) associated with the presence of the dioxo moiety in (V) and (VI) states. However, when fit to an arc tangent and 2 Gaussians (Fig. 9), which may be more sensitive to valence and less sensitive to the positions and shapes of the other features of the edge, the arc tangent (ionization) energies do increase progressively as the oxidation state increases. See the following equation:

$$\text{Fit} = k_0 + k_1 \cdot \arctan[k_2 \cdot (x - k_3)] \\ + k_4 \exp\left\{-\left[\frac{(x - k_5)}{k_6}\right]^2\right\} + k_7 \exp\left\{-\left[\frac{(x - k_8)}{k_9}\right]^2\right\}$$

when  $x$  is the x-ray energy in eV and  $k$  is a fit parameter.

Figure 9 shows an excellent linear correlation between the edge position and the plutonium oxidation state ( $r^2=0.997$ ).

Addition of a third Gaussian to the XANES deconvolution for the V and VI species affected the edge position only marginally (Table 6), and we still conclude that higher edge position correlates with higher oxidation state. Therefore, the second type of fit avoids interference from the “white line” when one is determining the energy of the edge.

These observations show that the primary determinants of plutonium XANES is the valence state and the presence or absence of the trans dioxo moiety, consistent with previous uranium and neptunium XANES studies.<sup>6-9</sup> This work establishes that XANES spectroscopy provides a rapid and straightforward means for determining the average valence of plutonium in species with primarily oxygen ligation, using a combination

of the spectral features (III and IV vs. V and VI) and the calculated arc tangent edge energy. We expect XANES to be a useful tool in the study of plutonium speciation, and we will continue this effort by measuring the XANES spectra of other series of plutonium complexes.

The XANES calibration curve for the aquo species of plutonium in the III, IV, V, and VI oxidation states reported here is based on fitting a limited number of data sets for each oxidation state. The reported error in the position of the arc tangent arises from the error in the fit. In order to evaluate the reproducibility of this approach for use in determining oxidation state, it would be useful to compare the position of the arc tangent using many data sets. Such a database exists.

Plutonium sorbed onto anion-exchange resins occurs only in the IV oxidation state. We had collected data from a set of 10 resins during the March/April run. The structure of each resin is different. The different resin structures may affect the EXAFS region of the spectra. These differences will not affect the oxidation state of the plutonium and therefore should not affect the XANES spectra. We collected 2 spectra for each of the 10 different resins.



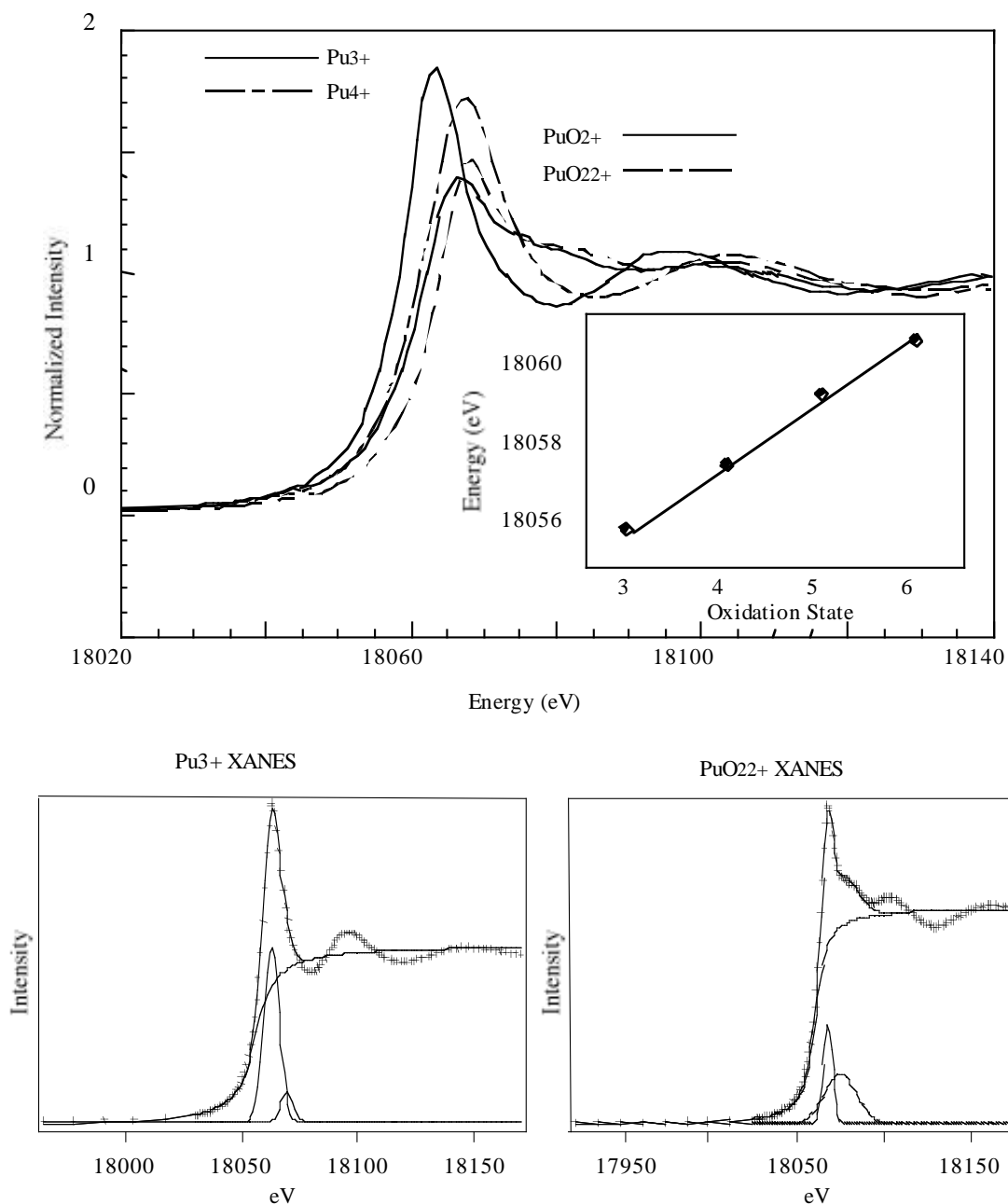


Fig. 9. (Top) Plutonium XANES spectra for the aquo (III) (IV), (V), and (VI) species. The edge energies, as measured by the inflection point of the arc tangent part of the fits, and the correlation with oxidation states are inset. (Bottom) Representative combined arc tangent and Gaussian fits of the XANES for Pu(III) and Pu(VI), representing the spherical and dioxo ions, respectively.

**Table 6. XANES Data for Plutonium Complexes\***

Sample	Second Derivative	Arc Tangent Edge	Arc Tangent Height	Arc Tangent Width	First Gaussian	Second Gaussian	Third Gaussian
Pu <sup>3+</sup>	18 059.6	18 055.8 ± 0.6	0.337 ± 0.007	0.17 ± 0.02	18 062.8	18 069.5	
Pu <sup>4+</sup>	18 062.7	18 057.6 ± 0.4	0.332 ± 0.006	0.19 ± 0.02	18 067.4	18 075.8	
PuO <sub>2</sub> <sup>+</sup>	18 062.1	18059.4 ± 0.3	0.326 ± 0.003	0.19 ± 0.02	18 065.5	18 071.6	
PuO <sub>2</sub> <sup>+</sup>	18 062.1	18 060.2 ± 0.4	0.327 ± 0.002	0.15 ± 0.01	18 065.7	18 072.1	18 099.8
PuO <sub>2</sub> <sup>2+</sup>	18 064.5	18 060.8 ± 0.2	0.322 ± 0.003	0.23 ± 0.02	18 067.9	18 075.2	
PuO <sub>2</sub> <sup>2+</sup>	18 064.5	18 062.0 ± 0.6	0.318 ± 0.004	0.20 ± 0.03	18 067.9	18 074.6	18 104.9

\*All energy positions are in eV, when the energy axis has been calibrated using the XANES edge from zirconium foil at 17 999.35 eV. The arc tangent height, width, and edge are taken from variables  $k_1$ ,  $k_2$ , and  $k_3$  respectively. See equation on p. 61.

The 20 spectra were fit with a single Gaussian and an arc tangent function. The average difference between the 2 spectra for each of the 10 resins was 0.03 eV, with both positive and negative values. This average difference indicates that no systematic error is in the database. The standard deviation in these differences is 0.18 eV and represents the reproducibility of the method for identical samples. The reported slope is 1.68 eV per oxidation state, and we assume that a mixture of oxidation states will be represented by an arc tangent position in an average position for the oxidation states. Thus, a reproducibility of 0.18 eV should allow one to distinguish between mixtures of oxidation states that are different by one-third of an oxidation state (three sigma). In other words, a mixture with an average oxidation state of 4 would be distinguishable

from a mixture with an average oxidation state of 4.33.

The standard deviation of the entire data set is 0.31 eV. The increase in the standard deviation of the entire data set compared with the standard deviation of differences in each sample may represent actual chemical differences between samples. However, the increase may represent a wider data variation that arises from changes in experimental conditions. This standard deviation represents an upper limit to the reproducibility of the method. Again, using three standard deviations, one should be able to distinguish between mixtures of oxidation states that are different by a little more than half an oxidation state.

The method, as it is described here, relies on energy calibration from a zirconium calibration sample with an

edge energy that is significantly different from the edge energy of plutonium. A plutonium metal calibration sample with an edge energy within a few eV of the samples would make the approach more robust and may increase accuracy. Such a plutonium calibration sample must be kept in an inert atmosphere to ensure that surface oxidation does not change the edge energy. We are pursuing this approach for future work.

We have acquired a Digital Equipment Corporation workstation and have loaded data analysis software. Data analysis for XANES and EXAFS work can be the limiting feature of these techniques. Because of the broad range of samples being studied, knowledgeable staff are required to obtain meaningful results. We are being trained on the data analysis software in order to more efficiently use this approach.

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***Core Technology: Actinide-Organic Interactions***

**Principal Investigators: Carol Burns and Steven McKee**

**Task Description.** The objective of this project is to explore the interaction of plutonium and other actinides with organic substrates. The actinide-organic interactions task was supported for six months beginning in April 1996. The schedule for FY96 involved two subtasks: aqueous actinide-organic chemistry and organoactinide chemistry. The Los Alamos National Laboratory team completed the readiness review for the operations. Unfortunately, a good retrofit of our glovebox optics well will require a group-level readiness assessment before any work can be performed in this glovebox.

**Status/Accomplishments.** The retrofit of the optics well has been and continues to be the stumbling block in our scientific efforts. The August 30 completion date indicated on the schedule, coupled with the recent planned facility shutdown, has forced the team to significantly revise the schedule for FY97.

No effort has been made to install the glovebox, beyond submitting the design change package for this action. Unfortunately, low priority in facility and infrastructure support has hampered scientific progress and will continue to do so.

The team has looked at a number of aspects of identifying residues for combustible technology demonstrations. We are trying to

prepare an experimental plan that will detail the questions that need to be explored and the science that will be needed to answer these questions. The team will investigate such interactions as solid-solid or surface contamination and solution interactions or complexation.

Studies associated with plutonium residues and solid organic matrices will focus on three types of organic materials: plastics, filter-type materials, and cellulose-type materials. These studies are specific to the task entitled “perform surface characterization experiments of actinide-entrained in organic matrices,” as listed in the *94-1 Research and Development Project Lead Laboratory Support Fiscal Year 1996 Technical Program Plan*.<sup>1</sup>

The questions that we want initially to address involve understanding the interactions between plutonium and the surface of materials. Is the interaction caused by impregnation of the plutonium residue into defects in the matrix? Or is the interaction caused by some adsorption mechanism, or even some chemical interaction; for example, by means of surface hydroxyl species? What is the chemical form of the plutonium—an oxide, an oxyhydroxide, or even a plutonium polymer? What is the particle size of the residue, and can the residue be chemically removed by a simple washing step? What happens

to these interactions in the presence of another material, such as tributylphosphate? These are the activities that we have begun at the end of FY96 and that will occupy significant time in FY97.

The lab for nonradioactive materials is ready for personnel to prepare some of the ligands necessary for the organoactinide chemistry work. Unfortunately, suitable gloveboxes in the Los Alamos Plutonium Facility Building PF-4 are not operational, including the inert glovebox that has the inert atmosphere capabilities necessary to perform this work. Unfortunately, the budget constraints

of FY97 have forced the team to forego this effort. The basic science component that was the driving force in the core technology program, i. e., basic science to expand the fundamental knowledge base of actinide chemistry, will not be realized.

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1. *94-1 Research and Development Project Lead Laboratory Support Fiscal Year 1996 Technical Program Plan*, Los Alamos National Laboratory publication LA-UR-96-991 (May 1996).

**Core Technology: Corrosion****Principal Investigator: Darryl P. Butt**

**Task Description.** Our objective is to correlate the effects of individual-grain crystallographic orientation (in polycrystalline alloys) with localized corrosion behavior of those grains. Our purpose is to discern the effect of surface structure on pitting and to gain insight into the stochastic nature of corrosion. Initially, we did a thorough literature review, selected materials (beryllium, nickel, titanium, and stainless steel), and prepared textured materials.

Los Alamos National Laboratory personnel have performed preliminary electrochemical tests on beryllium, nickel, and stainless steel. We are using orientation imaging microscopy (OIM) to map, before and after corrosion, the orientation of individual grains in polycrystalline metal samples. Our objective is to relate crystallographic orientation of specific grains to the tendency for localized corrosion as compared with general corrosion for those grains.

We collaborated with TexSEM Laboratories in Provo, Utah, for the initial work because OIM capabilities are not currently available at Los Alamos. Our OIM should be operable again in January 1997.

**Status/Accomplishments.** Stainless steel and beryllium are the two metals we examined using OIM during FY96. We wanted to determine the experimental procedure necessary

to permit coupling of OIM with corrosion studies. We also examined nickel alloys using bulk x-ray texture analysis to determine suitability for subsequent OIM/corrosion studies.

We examined the effect of crystallographic orientation on localized corrosion of 304 stainless steel in 4.1 M  $\text{HNO}_3$  + 1 M NaCl. We observed two distinct phenomena. First, upon initial immersion, the material actively dissolved, resulting in a partly faceted surface. Preliminary study of the sharply faceted grains suggested that the orientations of the grain faces were similar, being composed of the family of  $\{111\}$  planes. Second, pitting was observed following spontaneous passivation of the material. These pits were sharply faceted, displaying four-fold symmetry, and were found only within the sharply faceted grains. Clearly, both active dissolution and localized corrosion of 304 stainless steel exposed to 4.1M  $\text{HNO}_3$  + 1M NaCl display a crystallographic nature. We plan further study of this system.

We showed that OIM texture mapping of stainless steel is possible even with significant corrosion-induced topography. An example of the ability to relate corrosion properties to grain orientation is in Fig. 10, which demonstrates that pitting tends to occur in stainless steel in grains with  $\{110\}$  planes exposed to the surface

and generally avoids grains with {111} and, to some extent, {100} surfaces parallel to the sample surface.

OIM scans of the surface of beryllium yielded texture maps with a high degree of uncertainty. This effect seems to relate to sample damage that is localized near the surface during sample preparation (grinding and polishing), rather than to formation of an oxide layer. Alternative preparation methods are being investigated.

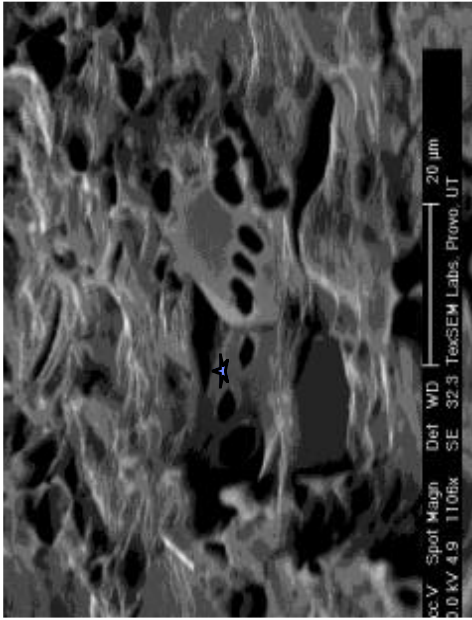
We performed preliminary electrochemical studies on the effect of texture on localized corrosion of nickel. To determine nickel's suitability for detailed study, we compared pitting susceptibilities of three different nickel 270 samples exposed to chloride environments. Each sample had a different processing history and texture. We performed three replicate potentiodynamic scans on each material to accurately determine the repassivation potential ( $E_{rp}$ ), a measure of the pitting susceptibility. The results of these tests suggested that one material had a significantly different  $E_{rp}$ . Statistical analysis confirmed that the  $E_{rp}$  of this material was indeed different from the other two nickel samples (confidence >99%). So, nickel appears to be a suitable material for study. The next step is the design of nickel 270 materials with specifically tailored textures.

Bulk x-ray texture analysis of nickel 200- and nickel 270-grade

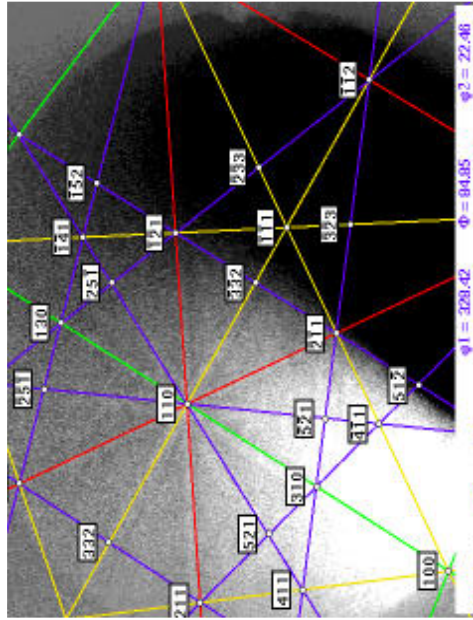
alloys indicates that various degrees and types of texture can be induced into nickel through readily available processing means. We have also demonstrated the ability to characterize texture in nickel by using OIM. This will permit a systematic study in this system through OIM/corrosion studies in samples with controlled and characterized textures.

In summary, in FY96 all milestones were completed on or ahead of schedule as follows:

- literature survey (complete);
- materials selection (phase I complete);
- fabrication of nickel, beryllium, and stainless steel samples (phase I complete);
- bulk texture analysis (nickel complete);
- texture mapping with OIM (beryllium and stainless steel phase I complete, nickel on hold);
- potentiodynamic polarization tests (beryllium, nickel, stainless steel complete);
- scanning reference electrode technology (systems set up, probes being redesigned); and
- demonstration of strong texture effects in beryllium, nickel, and stainless steel.



Indexed OIM pattern from marked grain





***Core Technology: Plutonium Diffusion Science***

**Principal Investigator: Pamela K. Benicewicz**

**Task Description.** In this project Los Alamos National Laboratory researchers are seeking to measure and to understand the diffusion of plutonium into materials at room temperatures and over long periods of time.

**Status/Accomplishments.** In FY96 we completed scoping studies to identify the appropriate surface-science techniques for determining the diffusion coefficient of plutonium in various metal matrices, including stainless steel. We chose two different techniques for the experimental determination of these diffusion coefficients: laser ablation spectroscopy and time-of-flight secondary ion mass spectrometry (TOF SIMS).

With both of these techniques, surface layers of metal materials that have been exposed to plutonium are removed, while plutonium concentration is simultaneously measured. With laser ablation spectroscopy, the depth profile is obtained by removing the layers material with a laser. With TOF SIMS, the layers are removed using ion beam sputtering. The resolution of TOF SIMS is  $\sim 50\text{\AA}$ , whereas the resolution of the laser ablation spectroscopy has yet to be determined. However, the laser system has the advantage of residing in the Los Alamos Plutonium

Facility. The TOF SIMS at the Los Alamos Chemistry and Metallurgy Research Building can only be used to evaluate very low radioactive-level samples. Finding the appropriate surface science instrumentation in a radioactive material-handling area was a recurring problem.

In FY96 we conducted a thorough literature search. Table 7 contains the self-diffusion coefficients for several phases of plutonium and uranium, as determined and published by six different authors. It is clear that both the phase of the material and the diffusion material itself heavily influence the diffusion coefficient. We used values in Table 7 and a straightforward model of the diffusion process in order to estimate the diffusion depths of the three different phases of plutonium at increasing times. As seen in Fig.11, diffusion depth is greatest for epsilon-phase plutonium; and the diffusion depth increases with increasing temperature, as expected.

We are collecting material for plutonium diffusion evaluation. Samples of beryllium, uranium, and stainless steel that have been in contact with plutonium for known periods of time are currently available for analysis. We sent beryllium samples to the Los Alamos analytical group in May for analysis, and we are awaiting the results.

Milestones in FY97 include initial sample analysis using TOF SIMS, optimization of the depth-profiling technique using the laser ablation system, initial sample analysis using laser ablation spectroscopy, and an interim comparison of the results

obtained by the two sample-analysis techniques. We plan a university collaboration whereby the plutonium diffusion process will be modeled in an in-depth manner. We will compare predicted results obtained with the initial model with the experimental results.

**Table 7. Variations of Diffusion Coefficient (D) with Phase of the Metal**

Host	Atom	Phase	$D_0$ ( $\text{cm}^2\text{s}^{-1}$ )	E (K cal mol <sup>-1</sup> )	D @ 300K ( $\text{cm}^2\text{s}^{-1}$ )
Pu	Pu	$\gamma$	$2.1 \times 10^{-5}$	16.7	$1.4 \times 10^{-17}$
Pu	Pu	$\delta$	$4.5 \times 10^{-3}$	23.8	$2.1 \times 10^{-20}$
Pu	Pu	$\epsilon$	$2.0 \times 10^{-2}$	18.5	$6.7 \times 10^{-16}$
U	U	$\alpha$	$2.0 \times 10^{-3}$	40.0	$1.4 \times 10^{-32}$
U	U	$\beta$	$2.8 \times 10^{-3}$	44.2	$1.8 \times 10^{-36}$
U	U	$\gamma$	$2.3 \times 10^{-3}$	28.5	$4.0 \times 10^{-24}$

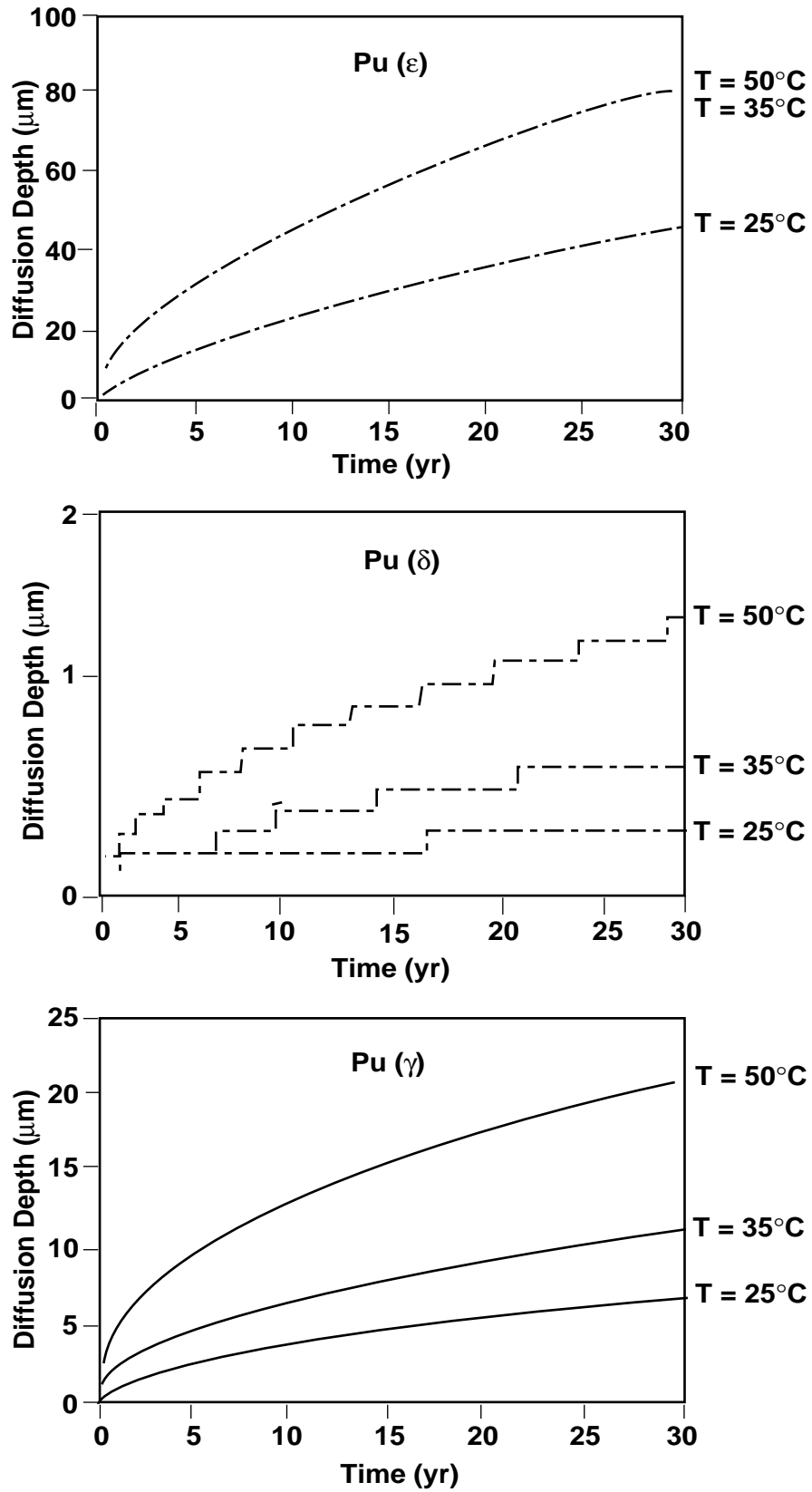


Fig. 11. Variations of the diffusion depth as a function of temperature and phase.

**Core Technology: Nondestructive Assay**  
**Principal Investigator: Teresa Cremers**

**Task Description.** As a plutonium metal sample oxidizes, alpha particles from the plutonium interact with oxygen nuclei to produce random (alpha-n) neutrons. These (alpha-n) neutrons increase the emitted neutron rate of the sample, and this change should be detectable using state-of-the-art neutron counting methods. Neutron counting methods, if they can be shown to be sensitive enough, should be ideally suited to this application because they are rapid and noninvasive. In addition, the same data collected for sample screening can also be reduced to a plutonium mass assay that can be used for material accountability.

Early in this project, Los Alamos National Laboratory researchers performed sensitivity calculations that showed that a high-efficiency neutron multiplicity counter may be able to detect as little as 1–2 g of plutonium oxide in the presence of 2000 g of metal. This sensitivity assumes reproducible sample positioning and a low, stable ambient neutron background. Measurements made in an actual plant environment could be considerably less sensitive if the neutron background and sample positioning cannot be well controlled. The purpose of this study was to investigate the sensitivity of neutron counting for this application in a real plant environment.

**Status/Accomplishments.** Two metal samples, each containing ~2kg of plutonium metal, were selected and measured with the in-plant neutron multiplicity counter (NMC) in the Los Alamos National Laboratory Plutonium Facility. This instrument has an efficiency of ~54%. Initial measurements indicated that the samples consisted of several pieces of metal. We made this assumption from the fluctuations in the measured total neutron emission when the sample was disturbed. If a sample is in pieces and these pieces are free to move in the can, their redistribution will change the neutron self-multiplication and, thus, the total neutron rate. The fluctuations from measurement to measurement initially observed with the multiplicity counter were too large to be accounted for by changes in background, counting statistics, or electronic fluctuations. At this juncture, we opened the samples and observed them to indeed be in pieces.

We measured the cleaned metals in the in-plant NMC. Then we reopened and brushed the samples. For each sample, the oxide removed by brushing was combined with the earlier-produced oxide, so as to total 5 g of oxide. We then returned this 5g to the sample and measured the sample at least twice in the multiplicity counter. Between each measurement, the samples were

removed from the instrument and deliberately disturbed in order to redistribute the metal in its container. We measured the neutron background before we measured the samples and repeated the process if we had reason to believe the room background may have changed. In addition, a pure plutonium oxide standard was measured in order to check instrument stability. Twice more we repeated the procedure of adding oxide and measuring the samples with the multiplicity counter. Additions totaled 10g and 20 g of oxide, respectively.

The data demonstrated that detection of oxidation in plutonium metal by neutron methods is possible for a single-piece metal sample. Neutron counting can be used to detect oxidation when about 1% of the plutonium is in oxide form. If the

metal sample is in several pieces that are free to redistribute themselves in the container, the sample's neutron counting characteristics change and mask the effect of oxidation on the neutron emission rates. In the case of a multiple-piece metal sample, known concentrations of impurities can be used to correct the neutron emission rates in order to achieve a 1% detection limit.

A detection limit of 1% for a 1-kg metal sample represents about 10g of plutonium oxide. This amount of weight change is easily measured with an analytical balance. Thus, monitoring plutonium metal samples for oxidation is more easily accomplished by gravimetric methods than by monitoring neutron count rates.

***Core Technology: Separations—Polymer Filtration***

**Principal Investigators: Gordon Jarvinen and Barbara F. Smith**

**Task Description.** The polymer filtration process will remove actinides to very low levels from solutions produced by stabilization operations. This process is performed in order to meet site-specific liquid discharge requirements.

**Status/Accomplishments.** Having completed the assembly of the laser fluorescence equipment, Los Alamos National Laboratory researchers are ready to evaluate the linear polyethyleneimine polymers we have prepared. This will allow us to do comparison studies with two of the commercially available polyamines. We have prepared potassium bromide thin films of our polymers with different metal loadings of europium.

We did a bench-scale optimization study on the synthesis of our very best polymer for plutonium and americium binding in order to improve the level of functionalization, to reduce the synthetic steps to make the synthesis amenable to pilot-scale synthesis, and to reduce the cost of synthesis. We were able to do all this and get a final product that had an even higher binding constant for americium/plutonium than we had been able to achieve in the beginning. We took the optimized procedure and then scaled it to a 1-kg batch. The material is ready for testing on real waste waters.

**Core Technology: Separations—Polymer Foams****Principal Investigators: Gordon Jarvinen and Betty S. Jorgensen**

**Task Description.** Los Alamos National Laboratory researchers are investigating polymer foams for use in recovery of radioactive species from waste streams. An investigation into the structural and flow characteristics of foams shows that they have properties superior to resin beads. Foam columns were prepared from chloromethylstyrene/styrene copolymers and sealed into glass ion-exchange columns. We prepared the foams using several different techniques and compositions. Cell sizes of the foam varied from about 10 mm to 100 mm. The results from this study are summarized below:

- Foams columns can withstand pressure differentials of at least 40 psi with no damage to the foam.
- Pore closure does not occur at 40 psi.
- Foam columns can dry out and be reused without reconditioning. Resin-bead columns require rehydration and may require repacking, if allowed to dry out.
- Flow rates can be tailored. The cell size and interconnecting pores of the foam can be controlled to obtain a desirable flow rate.
- Flow rates obtained with this technique are comparable to, or faster than, flow rates obtained

in resin bead columns. Similar flow rates can be obtained at lower pressures.

- Very little pH or ionic-strength effect has been observed on flow rates.
- Very little shrinkage or swelling is seen in sulfonated foams.
- Resin beads, such as Dowex 50™ (sulfonated polystyrene), may experience sufficient hydrostatic pressure, upon rehydration, to break glass columns.
- Foams are amenable to functioning with a wider range of actinide-selective ligands than are resin beads.
- Monophosphonated foams have been prepared for actinide uptake studies.
- Foams have proved to be robust and to be able to withstand harsh processing conditions, such as heating for extended periods in concentrated sulfuric acid.

Actinide uptake experiments have been postponed until early FY97 because of the temporary absence of necessary personnel. Since these experiments have been delayed, we proceeded with grafted polymerization of ligands to the foams. To date, we have successfully

grafted polymerized vinylphosphonic acid, a vinyl phosphonate ester, and vinylpyridine to chloromethylstyrene foams. The vinylphosphonates tend to result in low degrees of grafting, but when these vinylphosphonates are copolymerized with vinylpyridine, weight gains of about 50% have been obtained. We will test these foams for actinide uptake.

We are currently in the process of setting up a contract for a collaboration with Professor

Spiro Alexandratos at the University of Tennessee. Dr. Alexandratos is a renowned expert on ligand-functionalized polymers. The collaborative research will involve functionalizing foams with actinide selective ligands. This work will be an extension of an earlier collaboration in which we showed that mono- and diphosphonic acid ligands on foams exhibited better kinetics and metal uptake than resin beads with the same functionalities.



***Core Technology: Materials Science—Thermodynamics***

**Principal Investigator: Mark A. Williamson**

**Task Description.** The objective of the thermodynamics task is to study the phase behavior and thermodynamic properties of plutonium oxychloride ( $\text{PuOCl}$ ), americium oxychloride, and mixtures of alkali chloride salts and actinide oxychlorides. Plutonium and americium oxychloride are potential byproducts of the oxidation step of the salt distillation process.

**Status/Accomplishments.** Los Alamos National Laboratory personnel completed high-temperature Knudsen effusion mass spectrometer studies of the sublimation of  $\text{PuOCl}$ . We collected intensity-temperature data for plutonium trichloride ( $\text{PuCl}_3$ ) (g) and for its fragment species,  $\text{PuOCl}$  (g), and possibly for plutonium monochloride ( $\text{PuCl}$ ) (g) and for plutonium oxide ( $\text{PuO}$ ) (g) in the temperature range of  $825^\circ\text{C}$ – $1000^\circ\text{C}$ . The results of the experiment confirm

previous ideas that at least two vapor species, in addition to  $\text{PuOCl}$  (g), are present during the sublimation of  $\text{PuOCl}$ . The data show that two parent species contribute to the  $\text{Pu}^+$  fragment species in the spectrum. One parent species  $\text{PuCl}_3$  (g), while the other is probably either  $\text{PuCl}$  (g) or  $\text{PuO}$  (g). We will complete on-appearance potential experiments in order to establish the identity of the other parent species. Establishing the identity of the vapor species will make possible a detailed thermodynamic analysis of the sublimation chemistry of  $\text{PuOCl}$ .

We completed a literature search of the vaporization chemistry of the sodium chloride-potassium chloride system. The data will be used to supplement data that are collected for the studies of mixed alkali-halide  $\text{PuOCl}$ .

***Core Technology: Materials Science—Vitrification***  
**Principal Investigator: Gerald Veazey**

**Task Description.** Los Alamos National Laboratory researchers on this project will demonstrate a glovebox vitrification process in order to study the application of vitrification as an alternative to cementation in dealing with plutonium-contaminated waste materials.

**Status/Accomplishments.** We obtained and assembled the equipment to allow vitrification in containers that have a 5-in. diameter. We chose this size container in order to allow its insertion into a Rocky Flats Environmental Technology Site pipe component, if desired. We began nonradioactive experiments with this equipment on surrogate ash waste. We made two runs using a frit formulation developed at Pacific Northwest National Laboratory (PNNL). These runs were used to develop technique and familiarity with the equipment and allowed us to gain insight into how the level of the molten glass affects the homogeneity of the waste form, relative to the heating elements.

We completed design of the off-gas scrubber system and have nearly completed procurement of the equipment. This system will be evaluated and modified as necessary in the nonradioactive experiments. The design of the scrubber system for the nonradioactive glovebox system will be based on the data generated during these nonradioactive tests.

PNNL began work to develop the glass-frit formulation for waste on evaporator bottoms. Phase 1 of the statement of work led to a formulation for nominal composition of the most prevalent type of evaporator bottoms (lean residue). In this work, PNNL tested 20 frit formulations to establish the boundaries of acceptability. The performance standards against which the frit formulations were tested in the molten state were viscosity and electrical conductivity. The final waste form was tested for leach resistance using the toxicity characteristic leaching procedure and for physical durability using the Product Consistency testing (ASTM C1285-94). From these data an optimum frit formulation was chosen and verified against the same standards.

We completed characterization of all evaporator-bottom waste streams at the Los Alamos Plutonium Facility. These data are needed for Phase 2 of the PNNL work, during which time researchers will develop frit formulations to handle all such waste streams. PNNL will attempt to accomplish full coverage with a single frit formulation while maintaining maximum waste loading. However, the diverse composition of the waste streams may dictate that multiple formulations are necessary to keep waste loading maximized. In this case, a compromise will have to be made

in waste loading in order to gain the advantage of a single frit formulation.

We have completed the National Environmental Policy Act (NEPA)

review of this project. The project has been granted a categorical exclusion from the requirement to prepare NEPA documentation.

***Core Technology: Materials Science—Vitrification of Rocky Flats Incinerator Ash***  
**Principle Investigator: T. S. Rudisill, Savannah River Site**

**Task Description.** About 20000 kg of incinerator ash are being stored at Rocky Flats Environmental Technology Site (RFETS). Vitrification is one possible treatment technology to stabilize this material and produce a shippable waste form, allowing shipment to the Waste Isolation Pilot Plant or to potential disposal using the can-in-can approach with Defense Waste Processing Facility high-level waste glass.

An alternative strategy for disposition of ash residues is to recover plutonium in a form that is suitable for storage under the DOE's long-term storage standard for plutonium metal and oxide (DOE-STD-3013-94). The Savannah River Site (SRS) F-Canyon and FB-Line provide facilities for such a recovery, provided ash can be dissolved in a way so that plutonium oxide dissolves with the matrix and does not settle to the bottom of the dissolver located at F-Canyon. One method proposed to solubilize the plutonium oxide is to flux the ash with an alkali carbonate to form an oxide mineral with the plutonium incorporated into the mineral's structure. Work on this project is conducted at SRS.

**Status/Accomplishments.** An SRS-proposed vitrification demonstration using actual RFETS incinerator ash was delayed by a secondary mixed-waste concern that was raised by the South Carolina Department of

Health and Environmental Control (SCDHEC). Initially, the SC DHEC directed the Savannah River Technology Center to treat as a mixed waste all equipment and facilities that came in contact with off-gas from the vitrification process, when the equipment and the facilities are discarded or decommissioned. As a result of the liability associated with mixed-waste generation, no work could be begun. However, personnel obtained exemption from this direction by estimating the vanishingly small volatilization rate of heavy metals and hazardous organics from the ash. The present direction from the SC DHEC is to treat only the primary glovebox high-efficiency particulate air filter as a mixed waste when we discard it.

Since the demonstration with actual RFETS ash was delayed, SRS researchers performed experiments using a simulated ash. The composition of the simulated ash was based on the average of a range of compositions reported by T.C.Johnson.<sup>1</sup> The simulated ash was nominally 45% glass formers (silicon and boron oxides), 20% carbon, 15% transition metals, 10% alkali and alkaline earth elements, and 10% plutonium. Thorium and neodymium oxides were used as surrogates for plutonium and americium oxides, respectively. SRS personnel modified the composition of

the simulated ash to reflect the higher plutonium concentration in the samples of RFETS ash stored at SRS. The composition of the simulated ash is shown in Table 8.

SRS researchers used borosilicate and soda-lime-silicate glass formulations to demonstrate the vitrification of the simulated RFETS incinerator ash. The composition of the borosilicate glass was the basis for SRS vitrification options in the ash trade study that was conducted by the Nuclear Materials Stabilization Task Group of the DOE Office of Environmental Management.<sup>2</sup> For this composition, key glass additives were adjusted to the values shown in Table 9.

They based the soda-lime-silicate glass formulation on the composition shown in Table 10 using a 50 wt % ash loading (including carbon).

Researchers performed six 50-g melts to demonstrate vitrification of the simulated RFETS ash. They performed each experiment in a 100-mL alumina crucible. Before vitrification, the carbon was removed from the simulated ash using a slow temperature ramp or calcination at 800°C–900°C. Melt temperatures for the two formulations ranged from 1300°C to 1500°C, although the glasses probably melt at lower temperatures (1200°C or lower). Ash loadings, including the carbon content, were 40 wt%–50wt %. The crucibles were manually stirred one to three times while the glasses were at melt temperature. The glasses were poured from the crucible onto a stainless steel plate to produce rapid cooling.

**Table 8. Composition of Simulated RFETS Ash**

Oxide	Composition (Wt %)
Aluminum Oxide (Al <sub>2</sub> O <sub>3</sub> )	3.4
Americium Oxide (AmO <sub>2</sub> )	0.1
Boron Oxide (B <sub>2</sub> O <sub>3</sub> )	1.7
Barium Oxide (BaO)	1.1
Calcium Oxide (CaO)	4.1
Chromium Oxide (Cr <sub>2</sub> O <sub>3</sub> )	0.8
Cupric Oxide (CuO)	1.1
Ferric Oxide (Fe <sub>2</sub> O <sub>3</sub> )	5.6
Potassium Oxide (K <sub>2</sub> O)	0.8
Magnesium Oxide (MgO)	4.5
Manganese Dioxide (MnO <sub>2</sub> )	0.1
Sodium Oxide (Na <sub>2</sub> O)	1.1
Nickel Oxide (NiO)	0.5
Diphosphorus Pentoxide (P <sub>2</sub> O <sub>5</sub> )	0.1
Lead Monoxide (PbO)	0.9
Plutonium Oxide (PuO <sub>2</sub> )	11.3
Stannous Oxide (SnO)	0.1
Tantalum Oxide (Ta <sub>2</sub> O <sub>5</sub> )	0.3
Titanium Dioxide (TiO <sub>2</sub> )	1.7
Carbon (C)	18.9
Silicon Dioxide (SiO <sub>2</sub> )	41.9

**Table 9. Key Additives  
for Borosilicate  
Glass Formulation**

Oxide	Composition in Glass (Wt %)
SiO <sub>2</sub>	50
B <sub>2</sub> O <sub>3</sub>	8
Zirconium Oxide (ZrO <sub>2</sub> )	1
Na <sub>2</sub> O	9
Lithium Oxide (Li <sub>2</sub> O)	4
CaO	3

**Table 10. Soda-Lime-Silicate Glass  
Formulation**

Glass Component	Composition (Wt %)
Ash	50
SiO <sub>2</sub>	30
Na <sub>2</sub> O	15
CaO	5

Experimental conditions for each melt are summarized in Table 11a and 11b.

The glasses produced during the vitrification experiments were nonuniform in color and varied from brown to black. X-ray diffraction showed that all glasses were

amorphous, although Melt 2 contained a small amount of crystalline thorium oxide. Researchers observed a small metal sphere in two experiments (Melts 4 and 5), when melt temperatures of 1300°C were used. X-ray fluorescence identified the metal spheres as a nickel-copper alloy, which suggests the metals were reduced by residual carbon in the melt. The melts were very fluid, especially the glasses that were heated to 1500°C. The viscosity at this temperature was low enough that the high-purity alumina crucibles were pervious to the molten glass.

Using the borosilicate and soda-lime-silicate glass formulations demonstrated during FY96 as the starting point, SRS personnel will perform a statistically designed experimental program in FY97 in order to optimize the primary processing variables (liquidus temperature and viscosity) and glass durability. The program will consist of a series of (20–30) melts during which the frit and ash compositions are systematically varied in order to identify the range of acceptable processing conditions and glass durability. Researchers will vary key components in the ash to address the broad range of compositions reported for RFETS ash.

**Table 11. Experimental Conditions for Ash Vitrification****11a. Carbon Removal by Slow-Temperature Ramp**

	<b>Melt 1</b>	<b>Melt 2*</b>
Glass Formulation	Borosilicate	Borosilicate
Ramp for Carbon Removal	5°C/min	10°C/min
Hold Points	600°C/700°C	Not Applicable (N/A)
Time	1 h/1 h	N/A
Melt Temperature	1300°C	1500°C
Time at Temperature	1.5 h	3 h
Number Stirs	1	2

\*Melt 2 was performed to remelt the glass produced in the initial experiment when solids were observed during the glass pour.

**11b. Carbon Removal by Calcination**

	<b>Melt 3</b>	<b>Melt 4</b>	<b>Melt 5</b>	<b>Melt 6</b>
Glass Formulation	Borosilicate	Borosilicate	Soda-Lime-Silicate	Soda-Lime-Silicate
Calcination Temperature	900°C	900°C	900°C	800°C
Ramp 1	10°C/min to 600°C	10°C/min to 600°C	10°C/min to 600°C	8°C/min
Ramp 2	7.5°C/min to 1500°C	4°C/min to 1300°C	4°C/min to 1300°C	Not Applicable
Melt Temperature	1500°C	1300°C	1300°C	1500°C
Time at Temperature	2 h	3.25 h	2.33 h	2 h
Number Stirs	3	3	2	2

Using the simulated RFETS ash with the addition of thorium oxide, SRS personnel performed 15 experiments in order to form a mineralized thorium product that dissolves uniformly in nitric acid. In these experiments, the composition of the flux (sodium carbonate:potassium carbonate) and the ratio of ash to flux were varied. The majority of the solidified products consisted of two-to-three layers with thorium oxide

present in all layers (from x-ray diffraction data). However, as the ratio of sodium carbonate to potassium carbonate was decreased, the solidified products looked more homogeneous. We performed four experiments using just potassium carbonate as the fluxing agent. The products from the four experiments appeared to be a single, homogeneous layer.

A sample from one of the more homogeneous products was dissolved in order to determine whether the thorium had been solubilized. When the sample was placed in 8 M nitric acid, dissolution of the bulk matrix occurred almost immediately. Researchers observed no further dissolution of the residual solids after being heated and stirred for 1 h at 50°C and 80°C. We sampled the solution after the matrix had been stirred for 1 h at room temperature, 50°C, and at 80°C. After the solution cooled, it was filtered. Samples of the filtrate and of the residual solids were obtained. Results from scanning-electron-microscope analysis of the solid samples showed that thorium oxide was still present. The solution analyses have not been completed. However, the results from the solids indicate that the fluxing was not successful in incorporating all of the thorium oxide into the mineral matrix as a soluble species.

A review of the pertinent literature suggests that thorium may not have been a good surrogate for plutonium in this instance. Reports exist of soluble plutonium (V) and (VI) compounds that can be obtained from

the high-temperature fluxing of plutonium (IV) oxide with sodium oxide or sodium peroxide.<sup>3</sup> However, there is only a limited temperature range at which these compounds are stable. If the compounds are heated at a temperature higher than ~900 °C, the plutonium oxide re-forms. Small-scale experiments are in progress in an attempt to duplicate the results reported in the literature. If successful, a mixed sodium-plutonium oxide that is readily soluble in nitric acid should be obtained.

## References

1. T. C. Johnson, "Recovery of Plutonium from Incinerator Ash at Rocky Flats," Rocky Flats Plant report RFP-2520 (1976).
2. "Ash Residue End-State Trade Study," U. S. Department of Energy Idaho Operations Office Plutonium Focus Area technical report DOE/ID-10560 (October 1996).
3. J. J. Katz, G. T. Seaborg, and L. R. Morss, Eds., *The Chemistry of the Actinide Elements*, 2nd ed., Volume 1, (Chapman and Hall Ltd., New York, 1986), Vol.1.

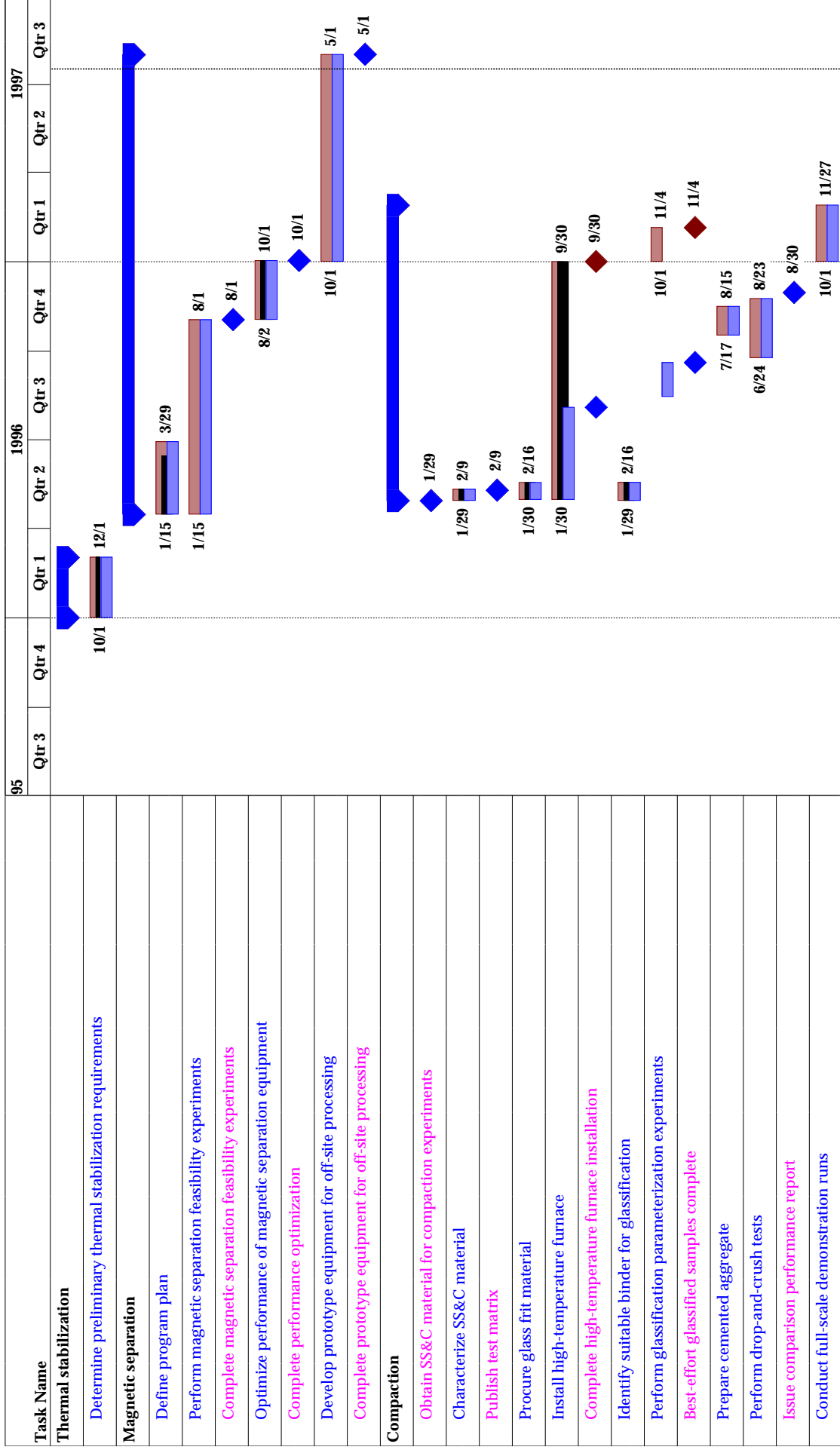




**APPENDIX:**  
**Detailed Work Schedules**



## Sand, Slag, and Crucible Stabilization



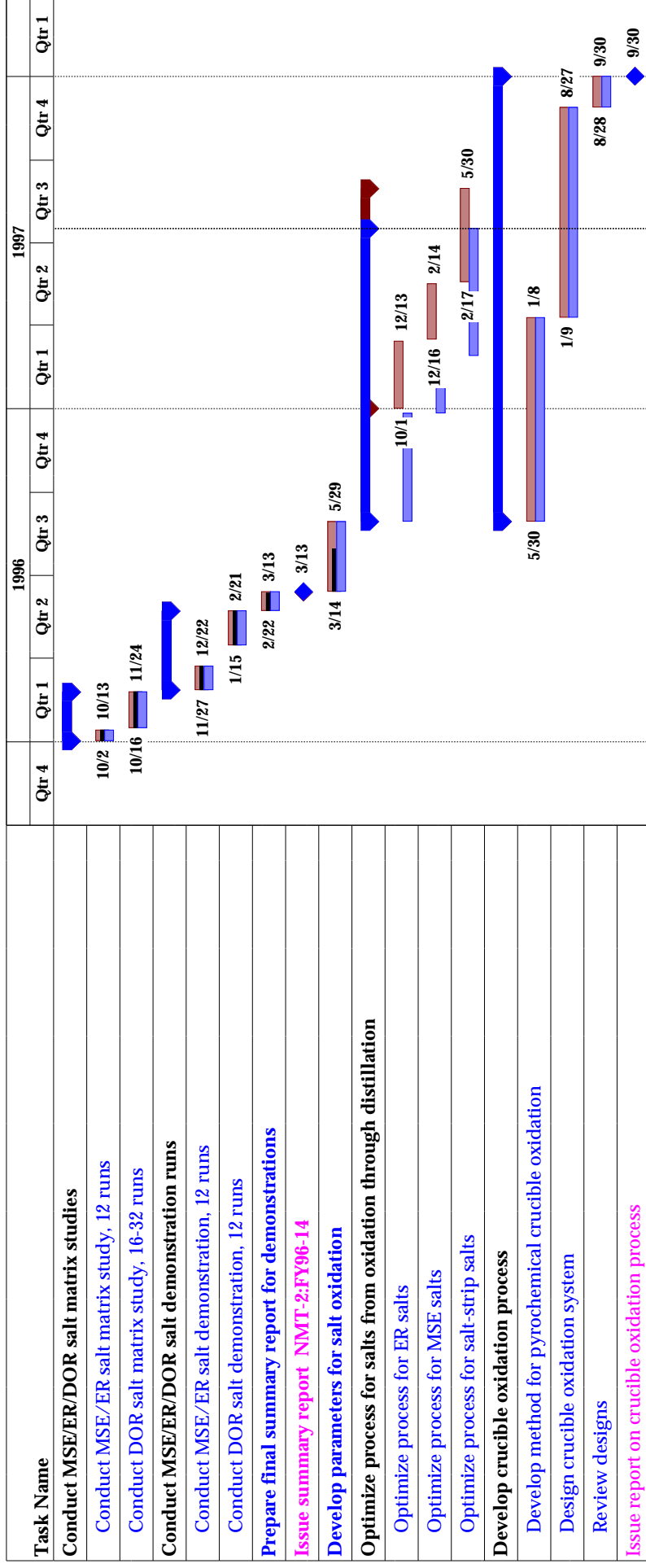
Task  
Progress

Baseline  
Milestone

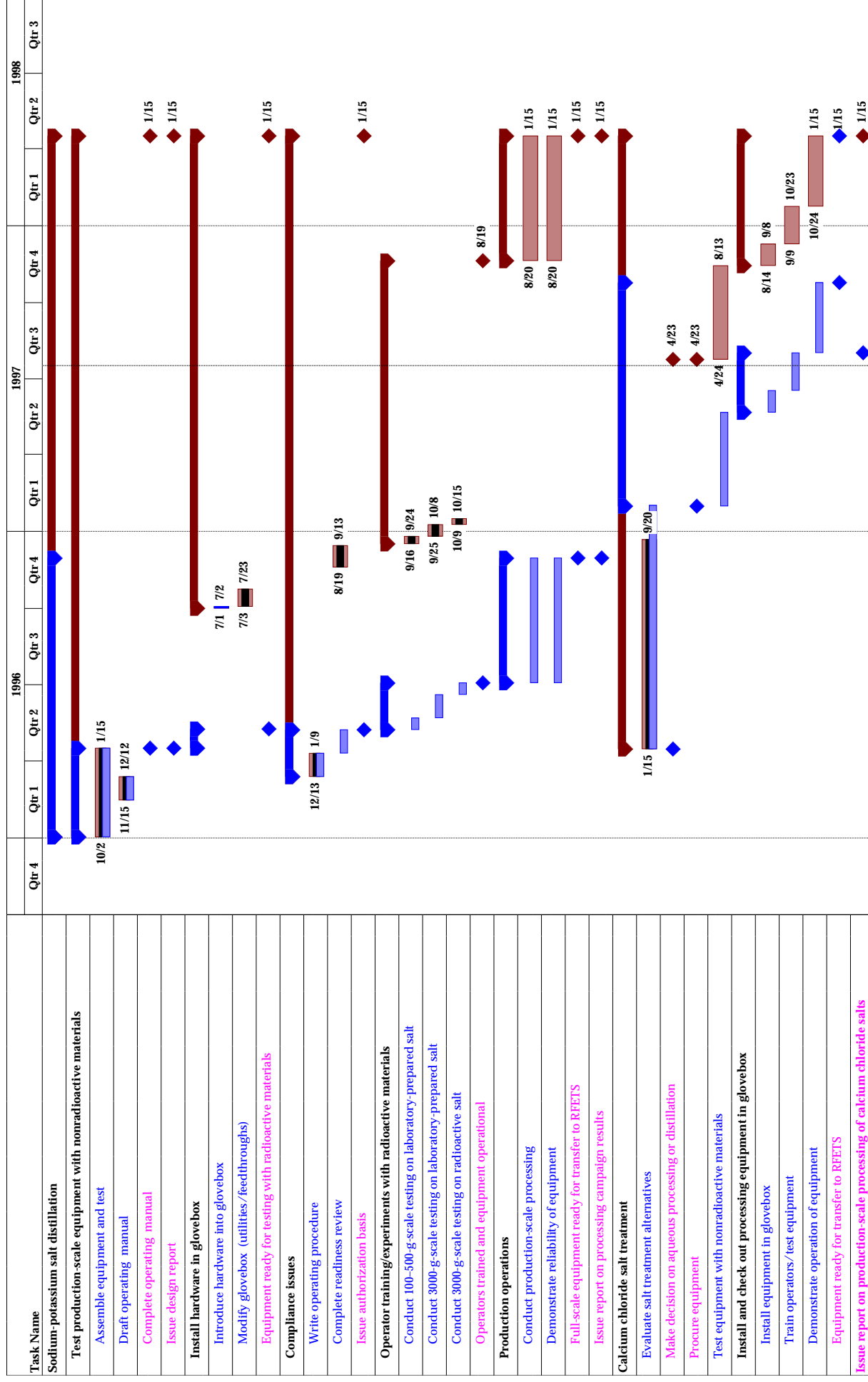
Baseline Milestone  
Summary

Baseline Summary

## Pyrochemical Salt Oxidation



## Salt Distillation

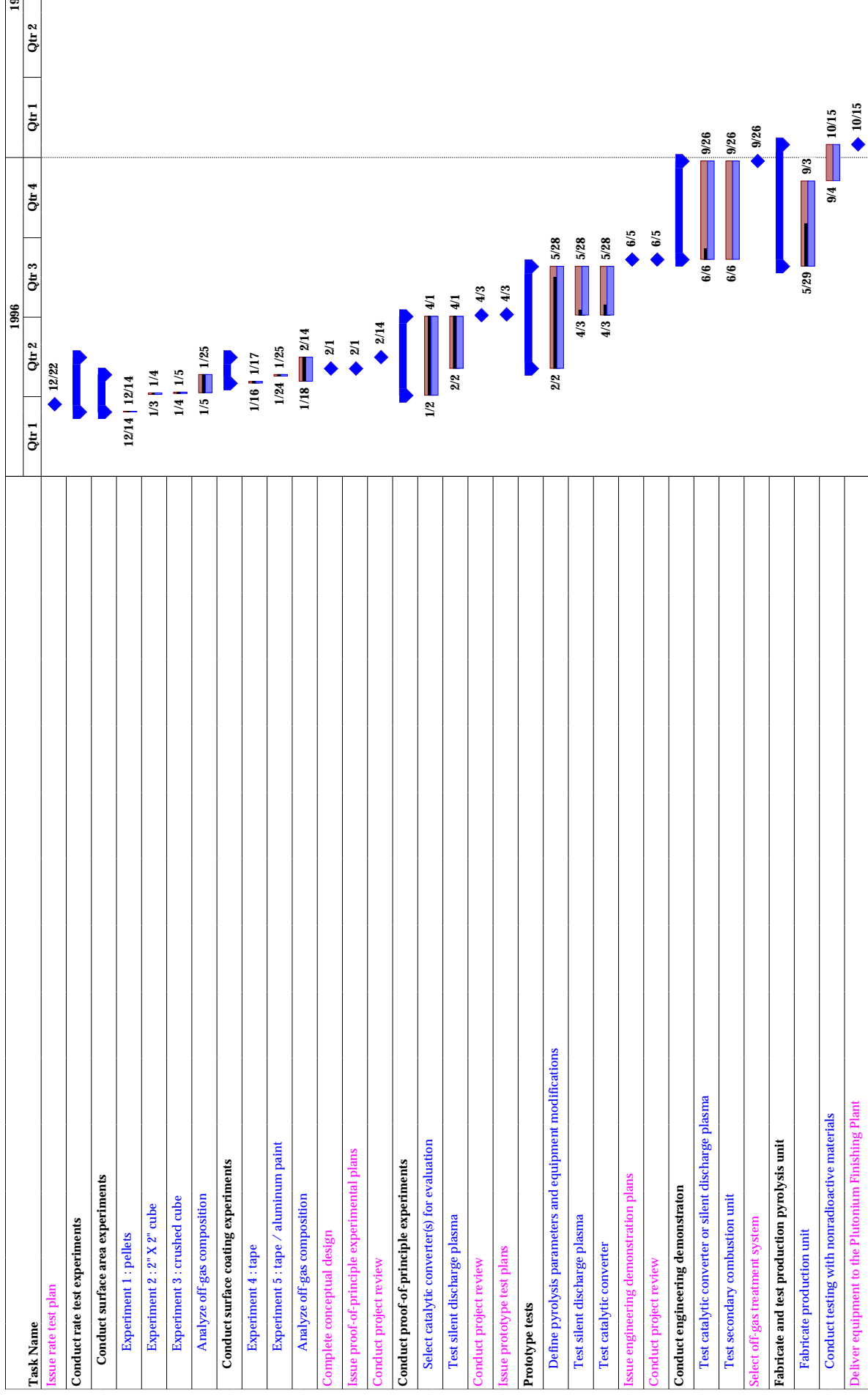


Task  
Progress

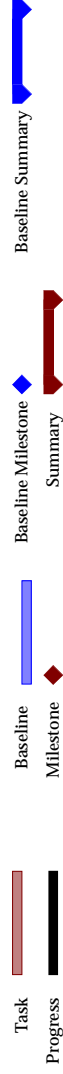
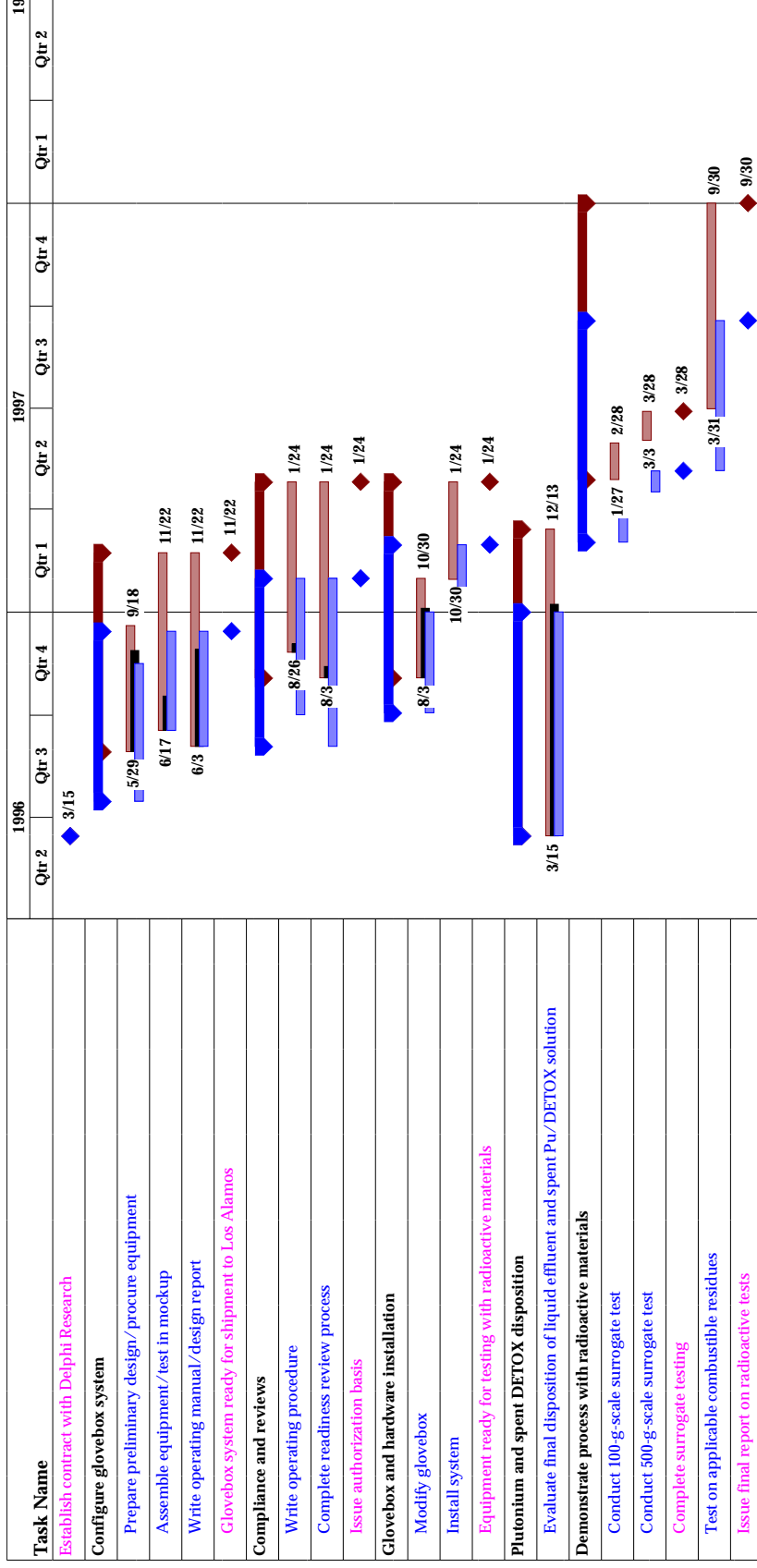
Baseline Milestone  
Summary

Baseline Summary

## Pyrolysis—Polycubes

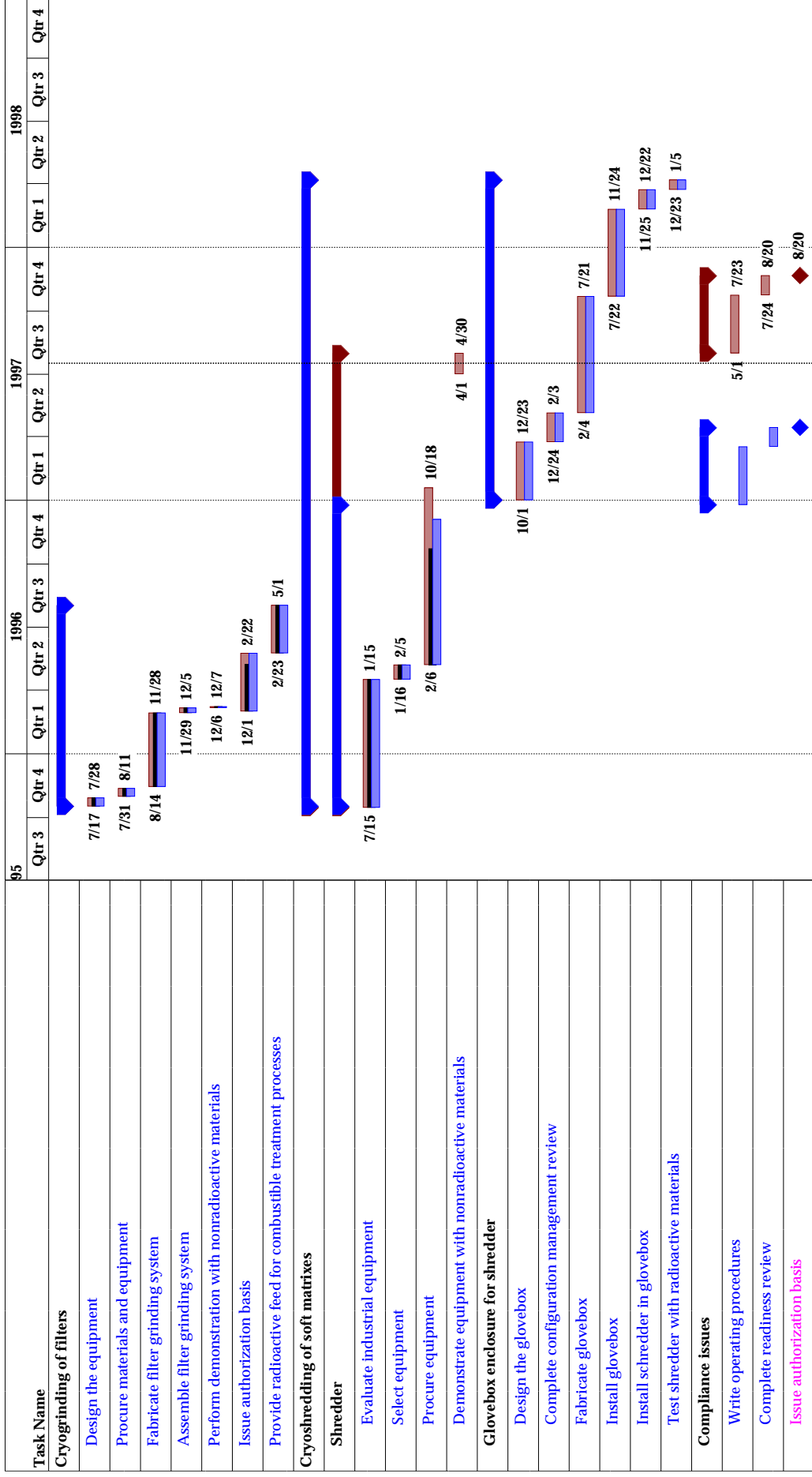


## Catalytic Chemical Oxidation

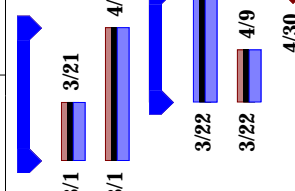
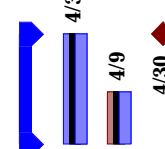






## Cryogenic Size Reduction



# Washing

Task Name	1996			
	Qtr 2	Qtr 3	Qtr 4	Qtr 1
<b>Planning</b>				
Complete experimental plan	3/1	3/21		
Complete literature search	3/1	4/17		
<b>Compliance issues</b>				
Complete safety assessment	3/22	4/30		
Review environmental issues	3/22	4/9		
Resolve safety and environmental issues		4/30		
<b>Nonradioactive experiments</b>				
Prepare surrogates				
Oil	3/22	4/10		
Oil/cerium	3/22	4/30		
Conduct surrogate experiments				
Oil	4/11	5/15		
Oil/cerium		5/16	5/30	
Issue report on nonradioactive experiments		5/30		
<b>Radioactive experiments</b>				
Install gloveboxes	3/22	6/14		
Conduct radioactive experiments		6/17	10/31	
Document results of radioactive experiments			11/1	11/29
Issue report on radioactive experiments				11/29

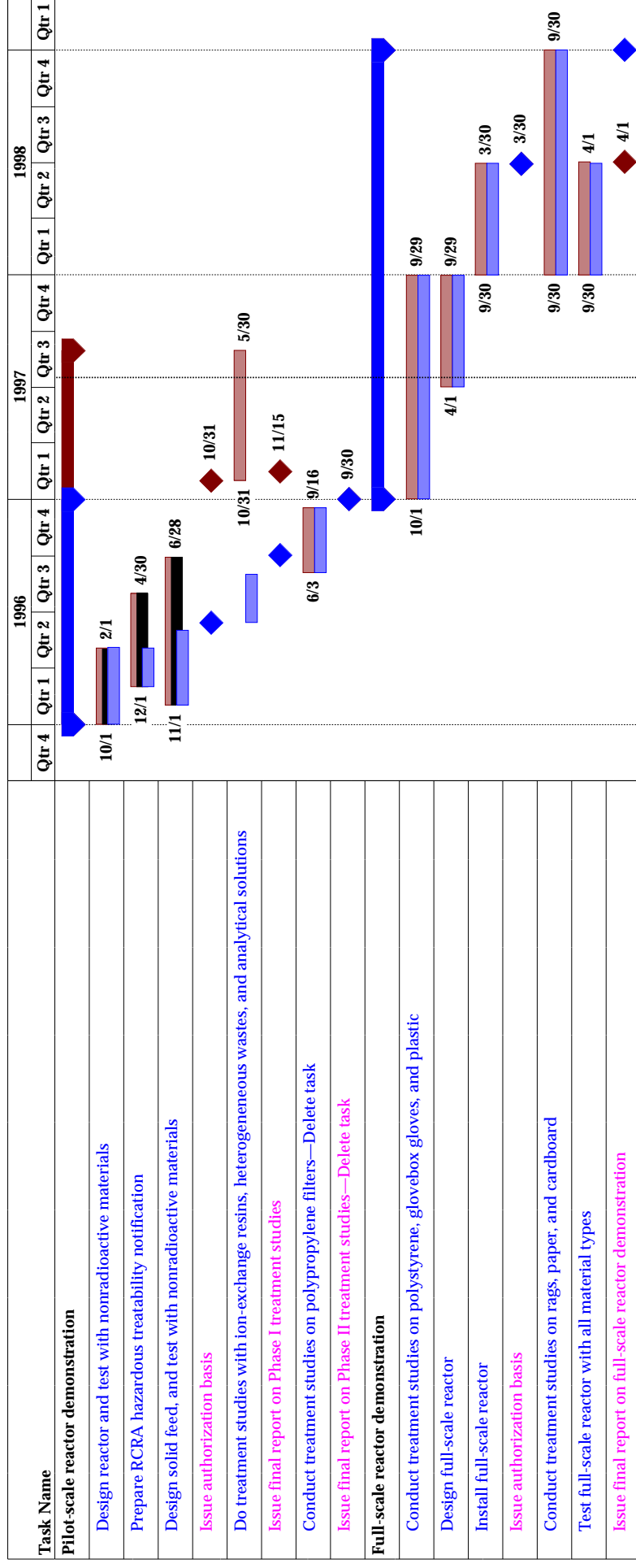
Task  
Progress

Baseline  
Milestone

Baseline Milestone  
Summary

Baseline Summary

## Hydrothermal Oxidation



Task  
Progress

Baseline  
Milestone

Baseline Milestone  
Summary

Baseline Summary

## Mediated Electrochemical Oxidation

Task Name	1996				19		
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2
Installation of electrochemical reactor	10/1	12/1					
Issue authorization basis			1/2				
RCRA hazardous treatability permit		12/1	2/1				
Conduct treatment studies on ion-exchange resins and analytical solutions		1/17		4/1			
Issue final report on phase I treatment studies				4/1			
Conduct treatment studies on polypropylene filters					4/1		
Issue final report on phase II treatment studies					9/16		
						9/30	

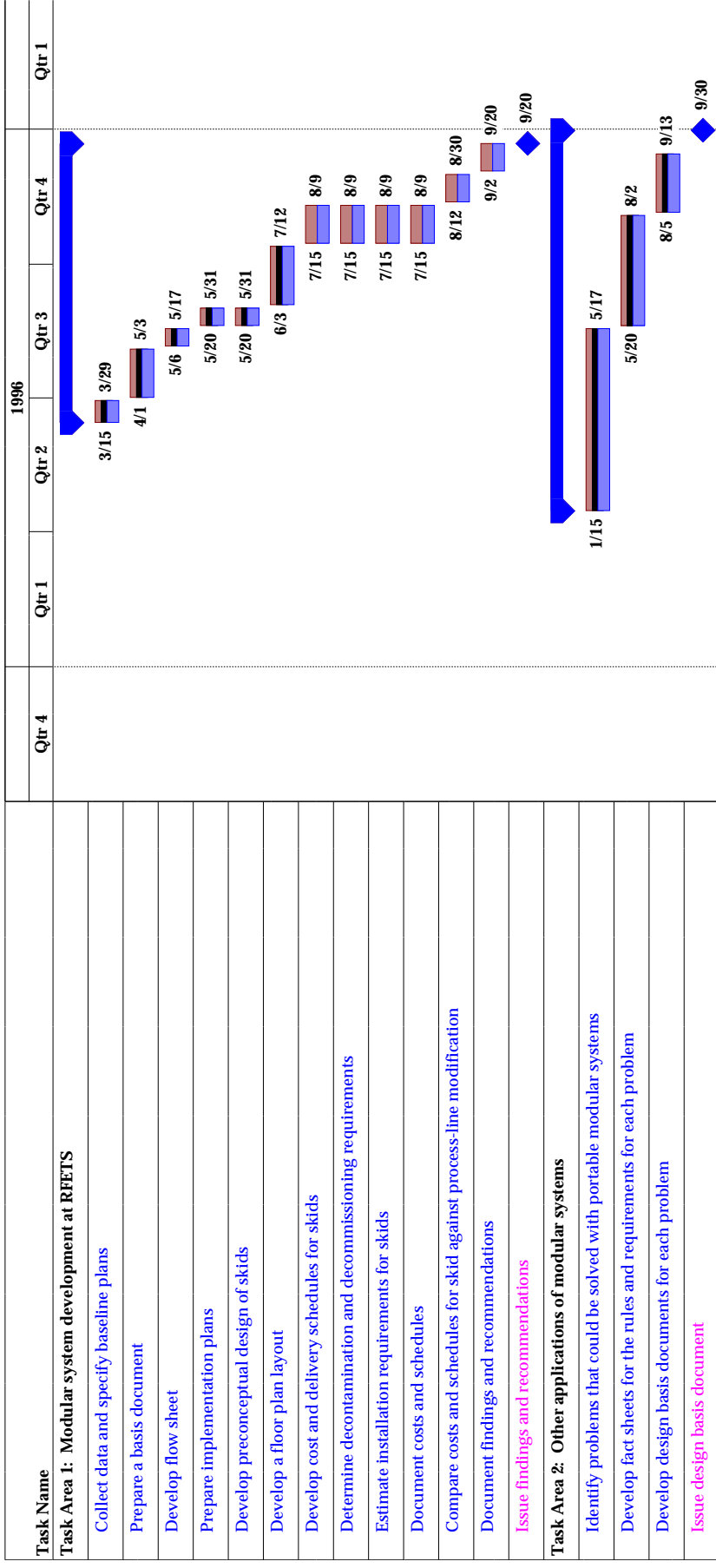
Task  
Progress

Baseline  
Milestone

Baseline Milestone  
Summary

Baseline Summary

## Modular Systems



## Electrolytic Decontamination Transfer System

Task Name	1996				1997				1998				
	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Prepare for demonstration with radioactive materials	10/1												
Conduct demonstration with radioactive materials													
Prepare final report on demonstration with radioactive materials		12/25											
Issue final report on demonstration with radioactive materials													
Design electrolytic decontamination system	11/15												
Install integrated system			4/2										
Demonstrate integrated system with radioactive materials						1/1							
Prepare final report on demonstration of integrated system						4/1							
Issue report on integrated system demonstration													
Initiate site-specific engineering and accomplish technology transfer													



Task  
Progress

Baseline  
Milestone

Baseline Milestone  
Summary

Baseline Summary

## Digital Radiography

Task Name	1996				19	
	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2
<b>Install and check equipment</b>	1/15		4/1			
Determine optimal operating parameters and applications						
Conduct statistical evaluation for precision bellows measurements		4/2		9/30		
Determine feasibility of weld evaluation		4/2		12/31		
<b>Place equipment in production operation</b>						
Determine feasibility of evaluating existing storage containers						
Conduct preliminary evaluation of existing vault containers			7/2		7/29	
Determine feasibility of detecting oxide corrosion products on metal			7/30		9/30	
Determine feasibility of detecting failed containers			7/30		9/30	

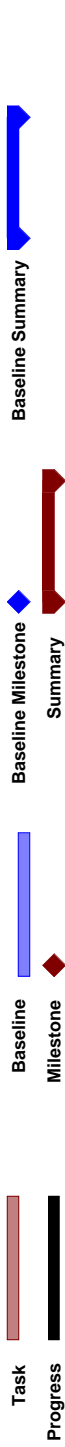
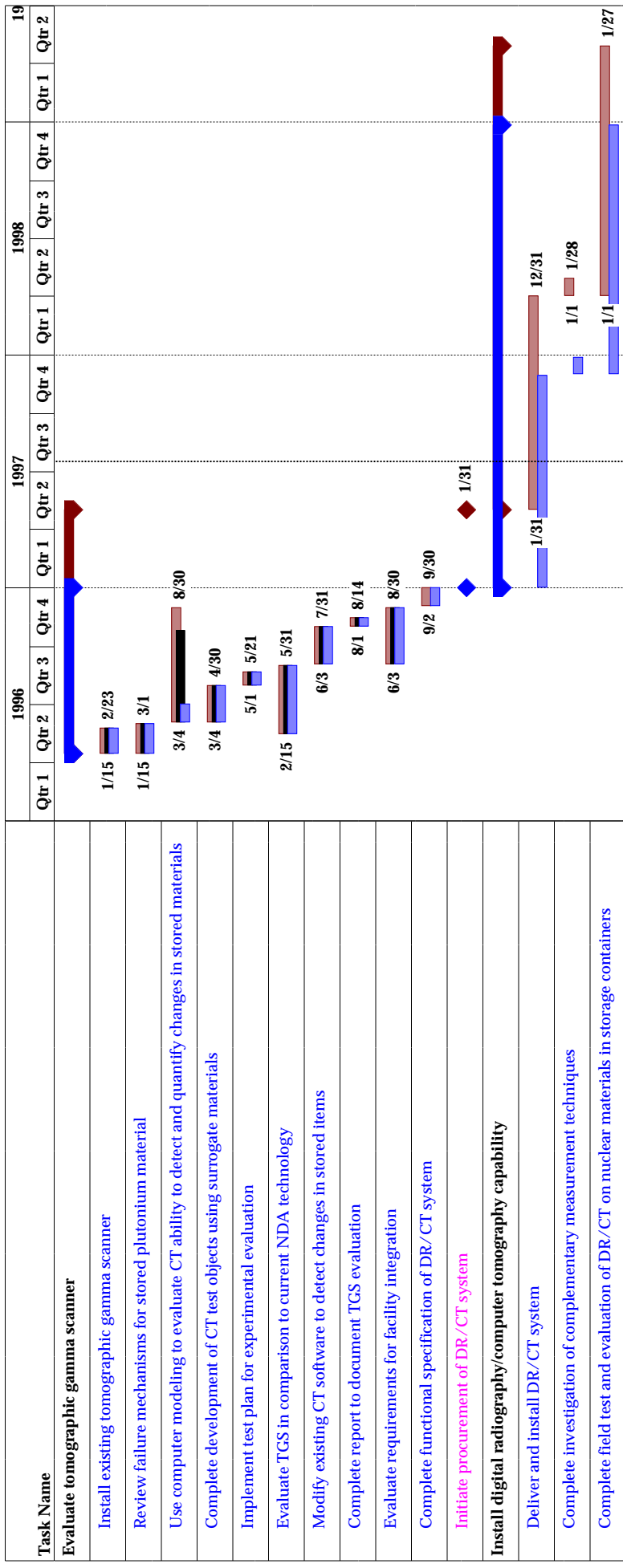
Task  
Progress

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Milestone

Baseline Milestone  
Summary

Baseline Summary

# Tomography





## Pressure-Sensitive Devices (Los Alamos)

Task Name	1996				1997				1998				1999	
	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2
SNL/NM and Los Alamos complete joint requirements definition	12/15	1/30												
Issue report on requirements definition		4/1												
Develop and fabricate sensor (SNL/NM)														
Quantify operating environment		1/31												
Modify and package sensor				8/19	9/30									
Review design (SNL/NM and Los Alamos)			5/14	9/30										
Assemble components				10/1	11/28									
Test integrated system					11/29	12/24								
Deliver hardware to Los Alamos														
Test first-generation sensors														
Conduct shelf-life studies using prototype gas, temperature, and pressure sensors														
Use experimental data feedback to modify devices														
Develop and improve oxygen sensor														
Conduct experiments with oxygen sensor														
Develop total pressure sensor														
Los Alamos conduct experiments with improved sensors														
Issue progress report on pressure sensitive devices.														

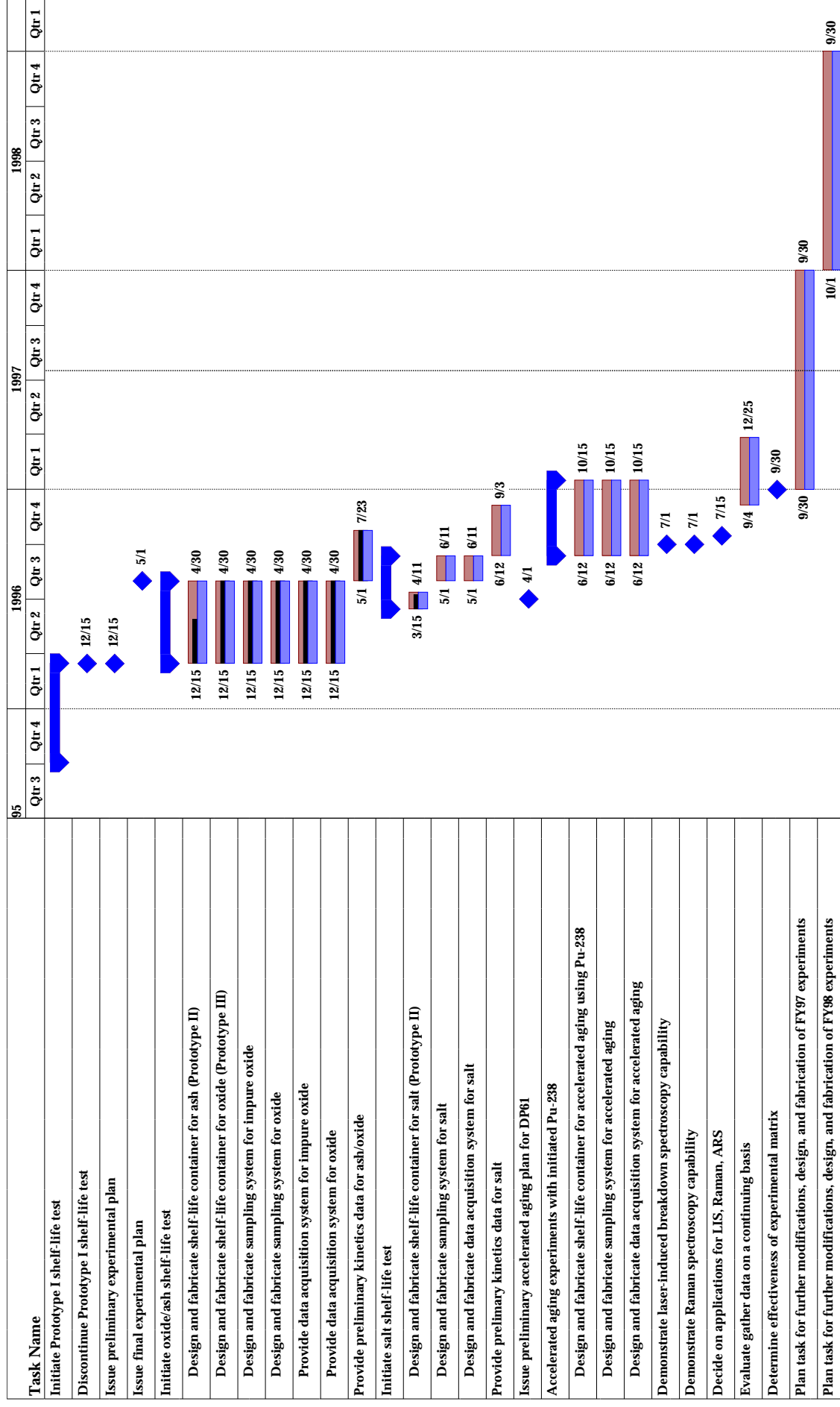
Task  
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Summary

Baseline Summary

## Metal, Oxide, Residue Shelf-Life Program



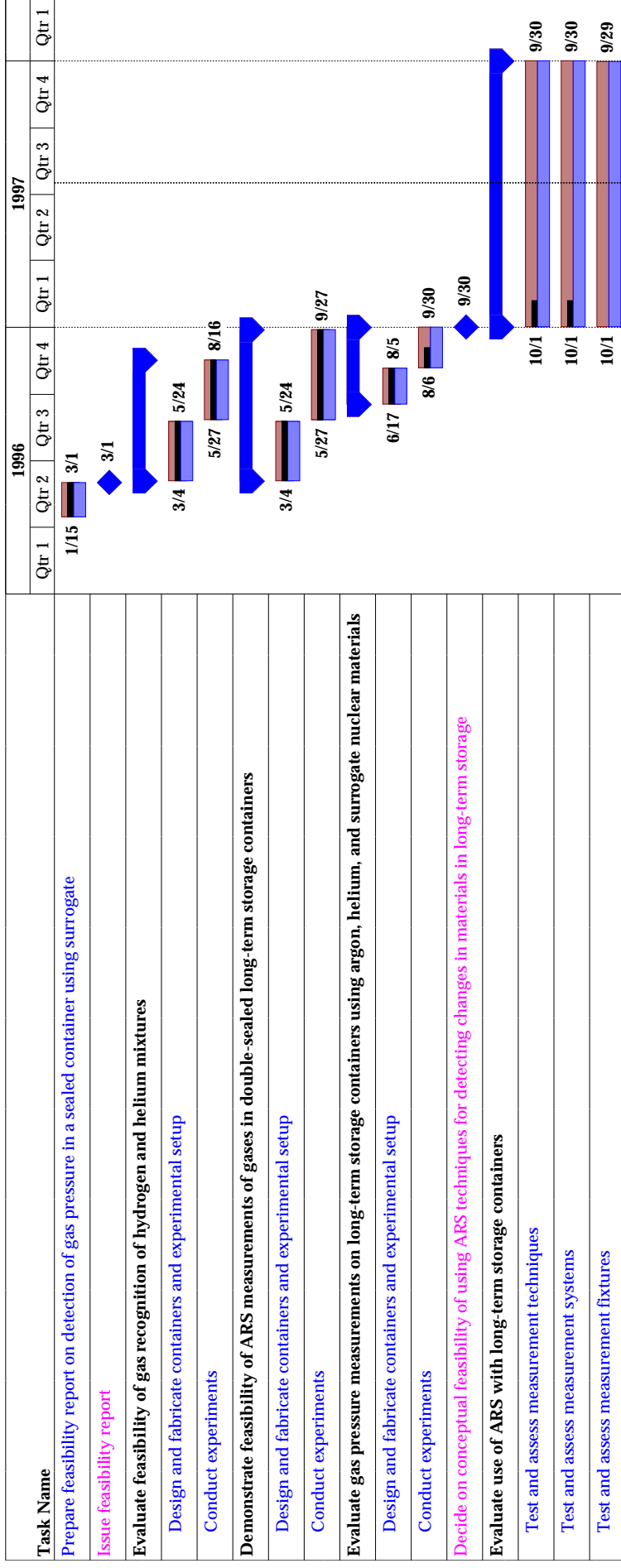
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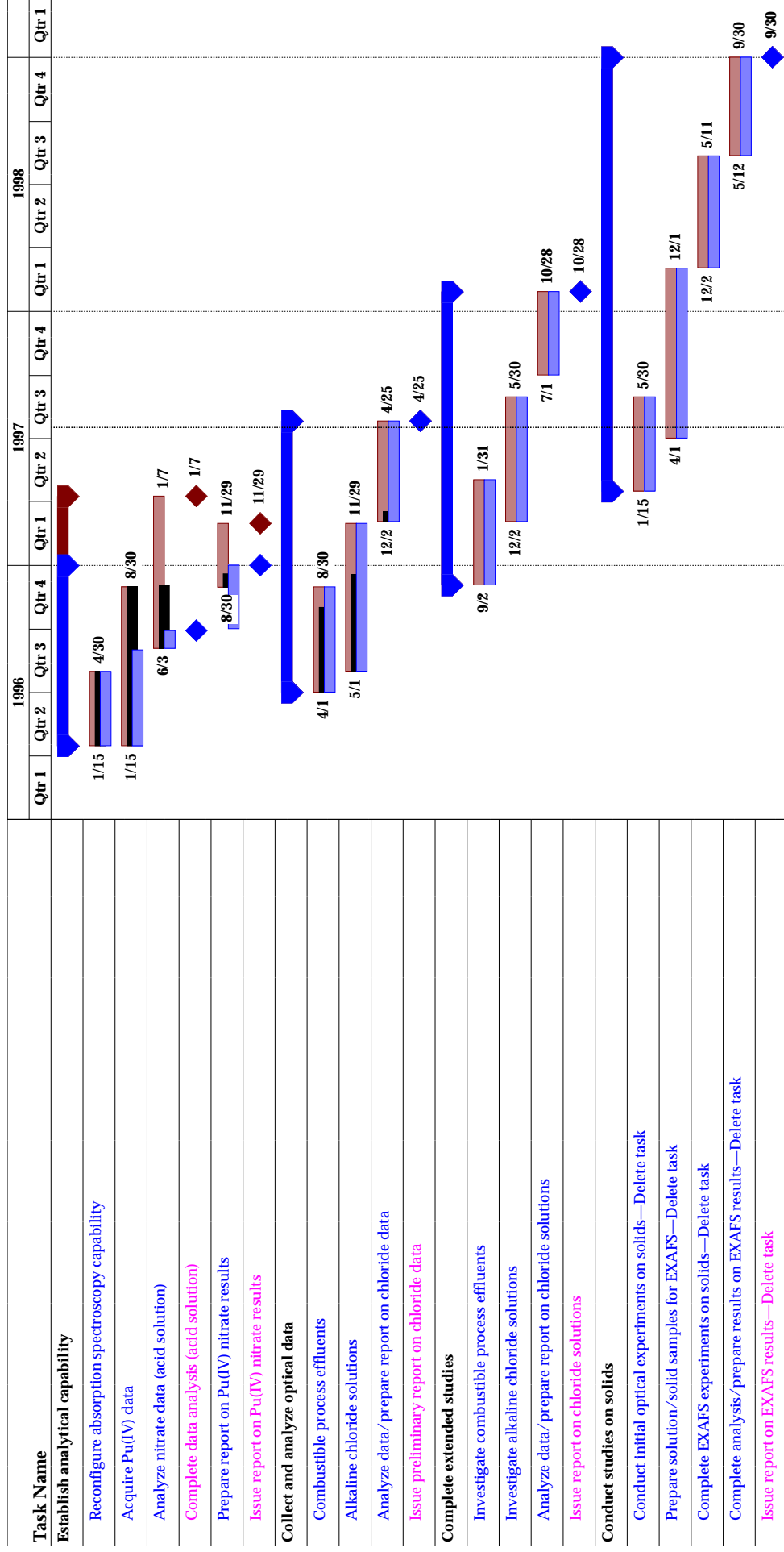
Baseline Milestone  
Summary

Baseline Summary

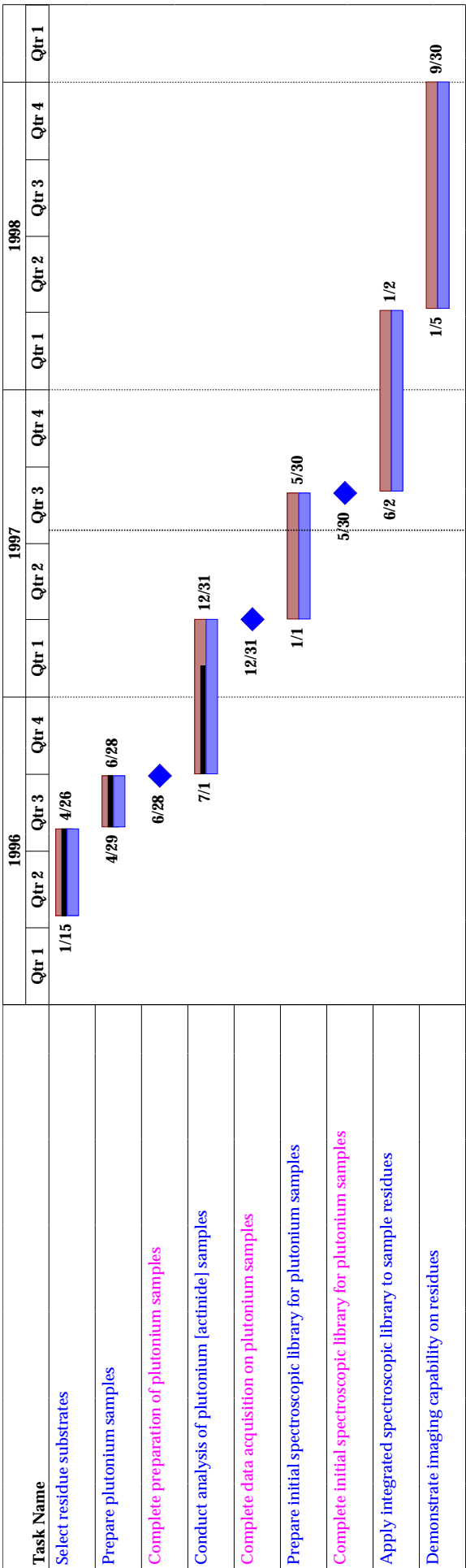
## Acoustic Resonance Spectroscopy



# Actinide Solution Chemistry (Los Alamos)



# Chemical and Physical Interactions of Actinides with Surfaces



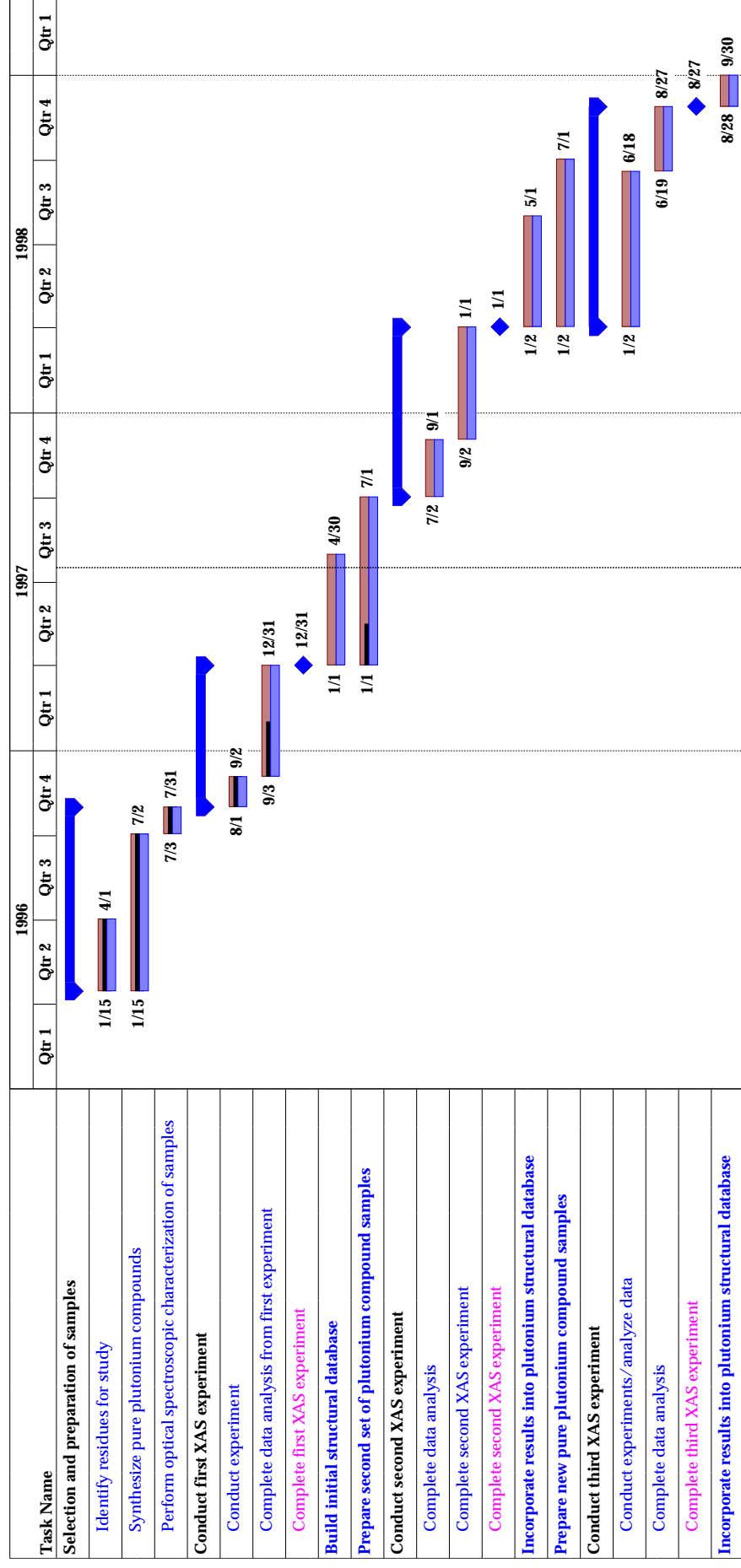
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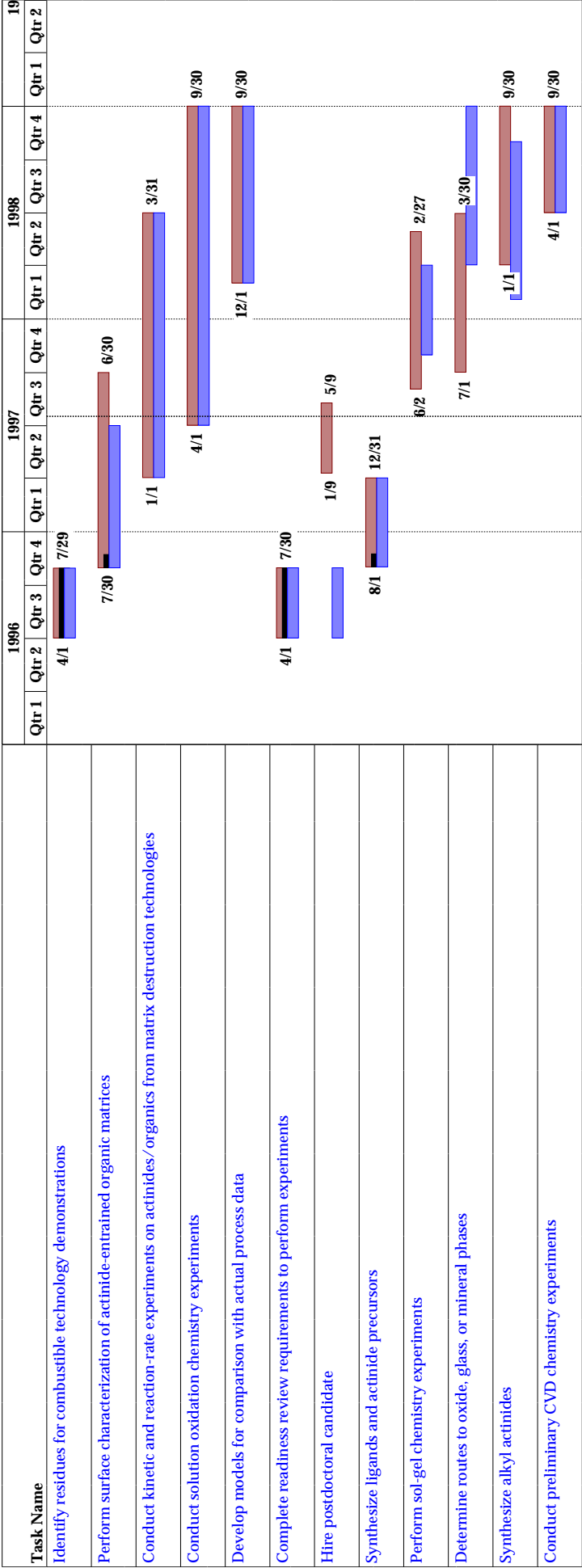
Baseline Milestone  
Summary

Baseline Summary

## Changes in the Chemical State of Plutonium



# Actinide-Organic Interactions



## Corrosion

Task Name	1996				1997				1998			
	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Complete literature survey		3/13	4/30									
Select material for study		5/1	5/30									
Conduct texture-mapping tests		5/31										
Conduct potentiodynamic polarization tests		8/1										
Conduct impedance spectroscopy tests		9/2										
Report on first year's results				10/31								
Conduct SRET tests of common polycrystalline engineering materials				11/4								
Conduct SRET tests on single-crystal orientations of interest					1/30							
Superimpose maps of texture onto maps of corrosion							8/1					
Report on second year's results								10/31				
Conduct SRET tests of textured polycrystalline engineering materials								11/3				
Report on third year's results												11/2

Task  
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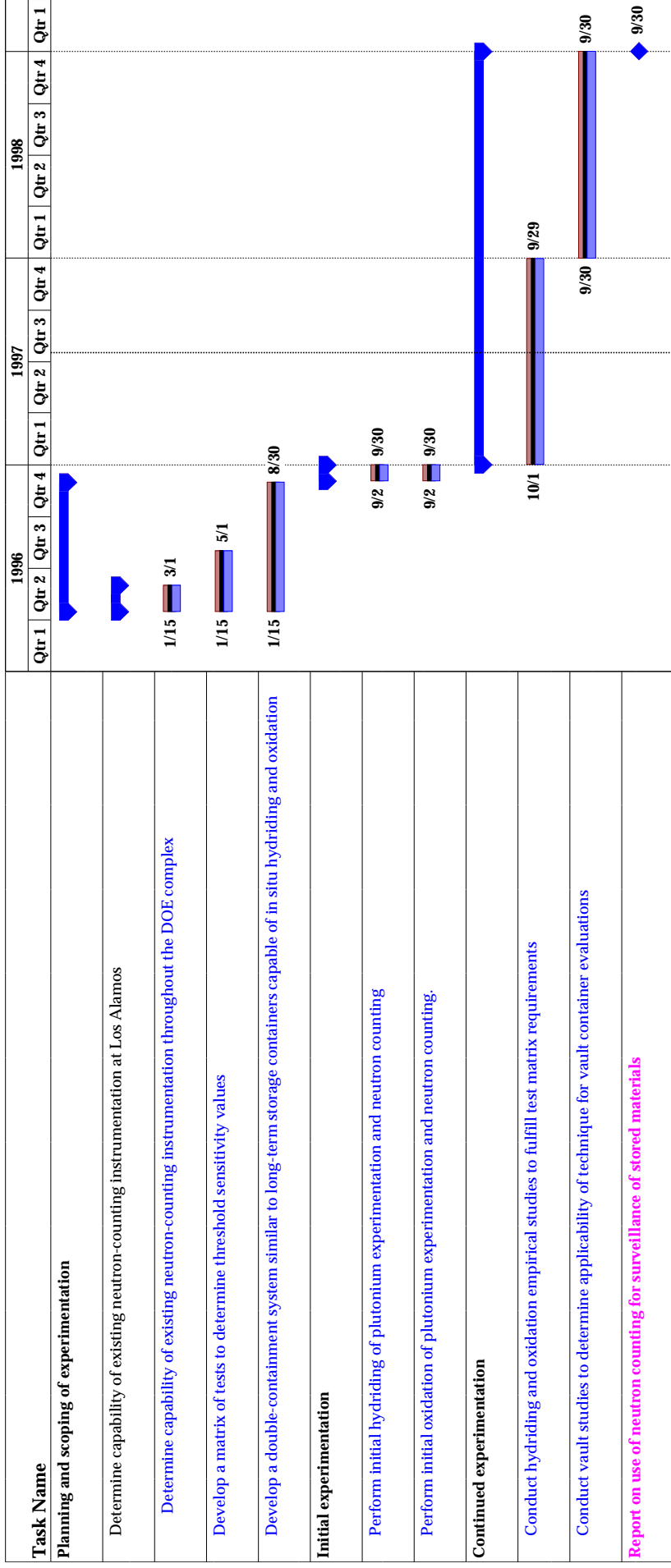


# Plutonium Diffusion Science

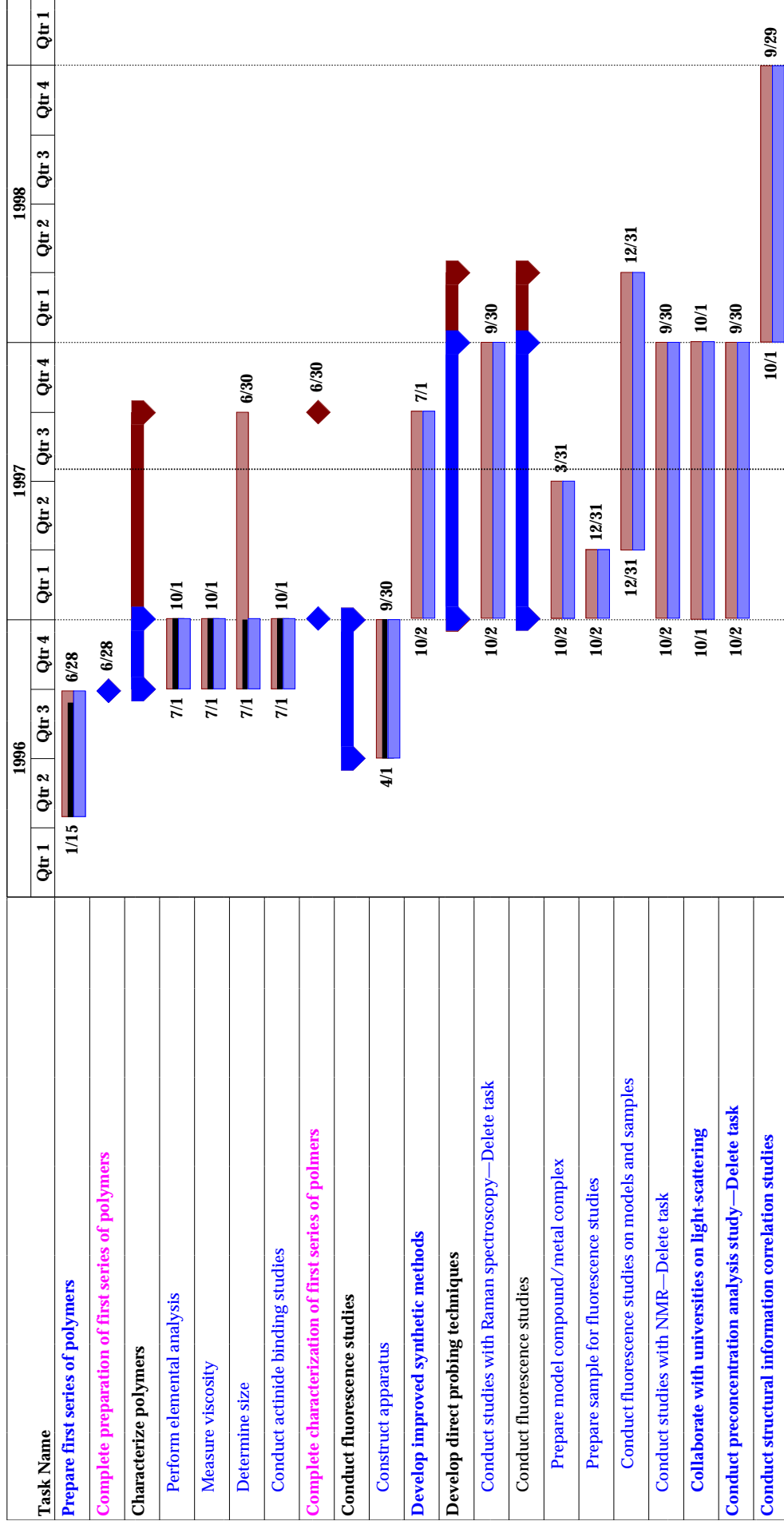
Task Name	1996				1997				1998			
	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Search the literature	1/15		4/30									
Develop experimental plan												
Select materials for study		5/1										
Select surface science analytical techniques		5/1										
Schedule experiments		5/1										
Issue experimental plan						9/30						
Conduct diffusion science experiments												
Issue report on first series of diffusion science experiments												



## Nondestructive Assay—Surveillance of Plutonium



## Polymer Filtration



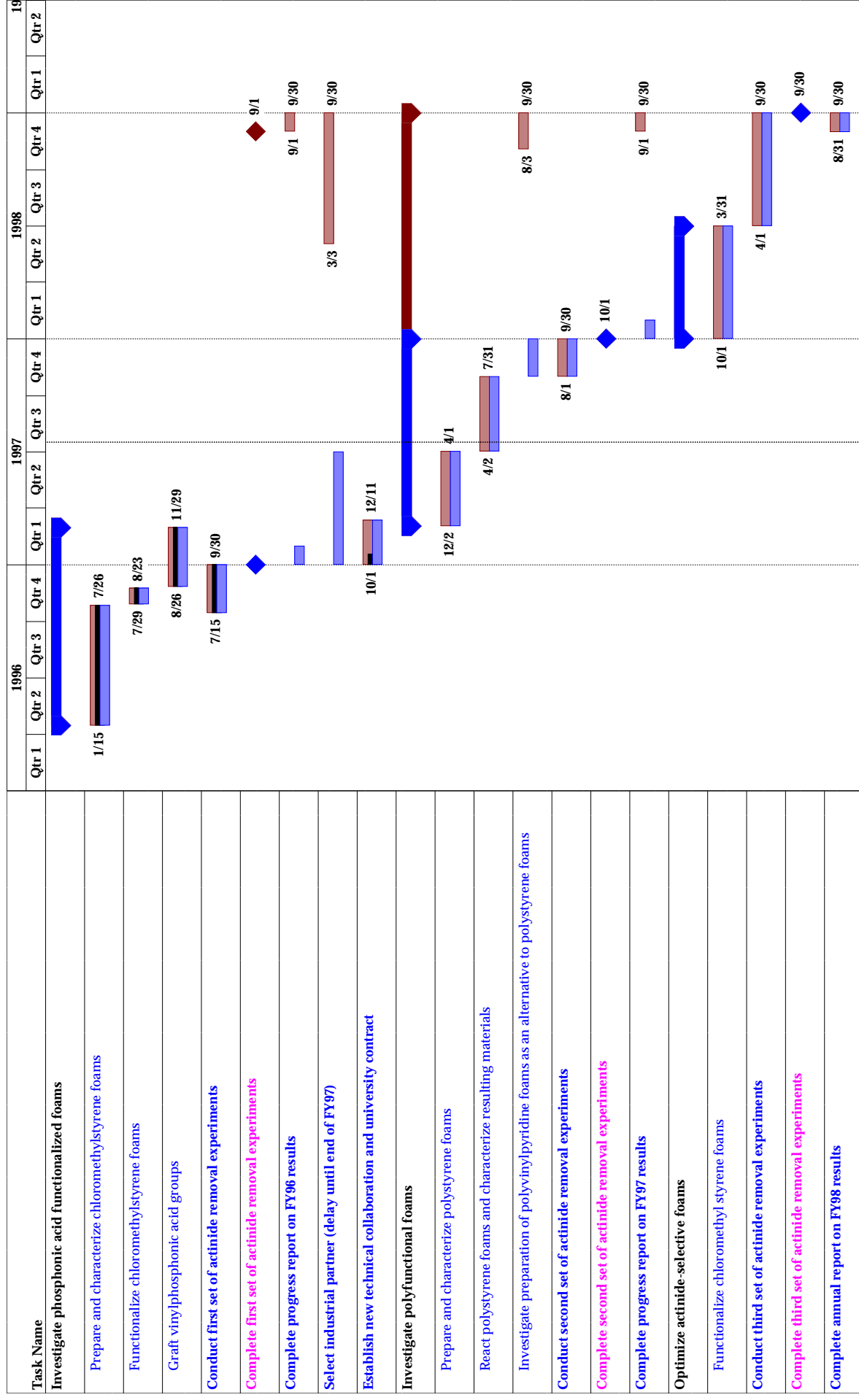
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Progress

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Milestone

Baseline Milestone  
Summary

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## Polymer Foams



## Thermodynamics

Task Name	1996				1997				1998			
	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4
Conduct experimental studies on PuOCl sublimation and vaporization	1/15		7/26									
Conduct experimental studies on AmOCl sublimation and vaporization				11/21	1/29							
Develop report on thermochemistry of PuOCl and AmOCl				1/30	4/1							
Issue PuOCl and AmOCl report							4/1					
Conduct experimental studies on mixed alkali halide/actinide oxyhalide salt mixtures			8/1	11/20								
Report on modeling of salt distillation processing				11/21	1/29							
Issue salt distillation modeling report						1/29						
Conduct vaporization studies on Pu-Zr silicate (zircon) solid solutions					2/28			8/28				
Prepare report on phase stabilities of zircon materials							5/23	8/28				
Issue zircon phase stabilities report								8/28				
Complete vaporization studies on Pu and Am oxides and issue report								8/29				9/29
Issue vaporization studies report												9/29

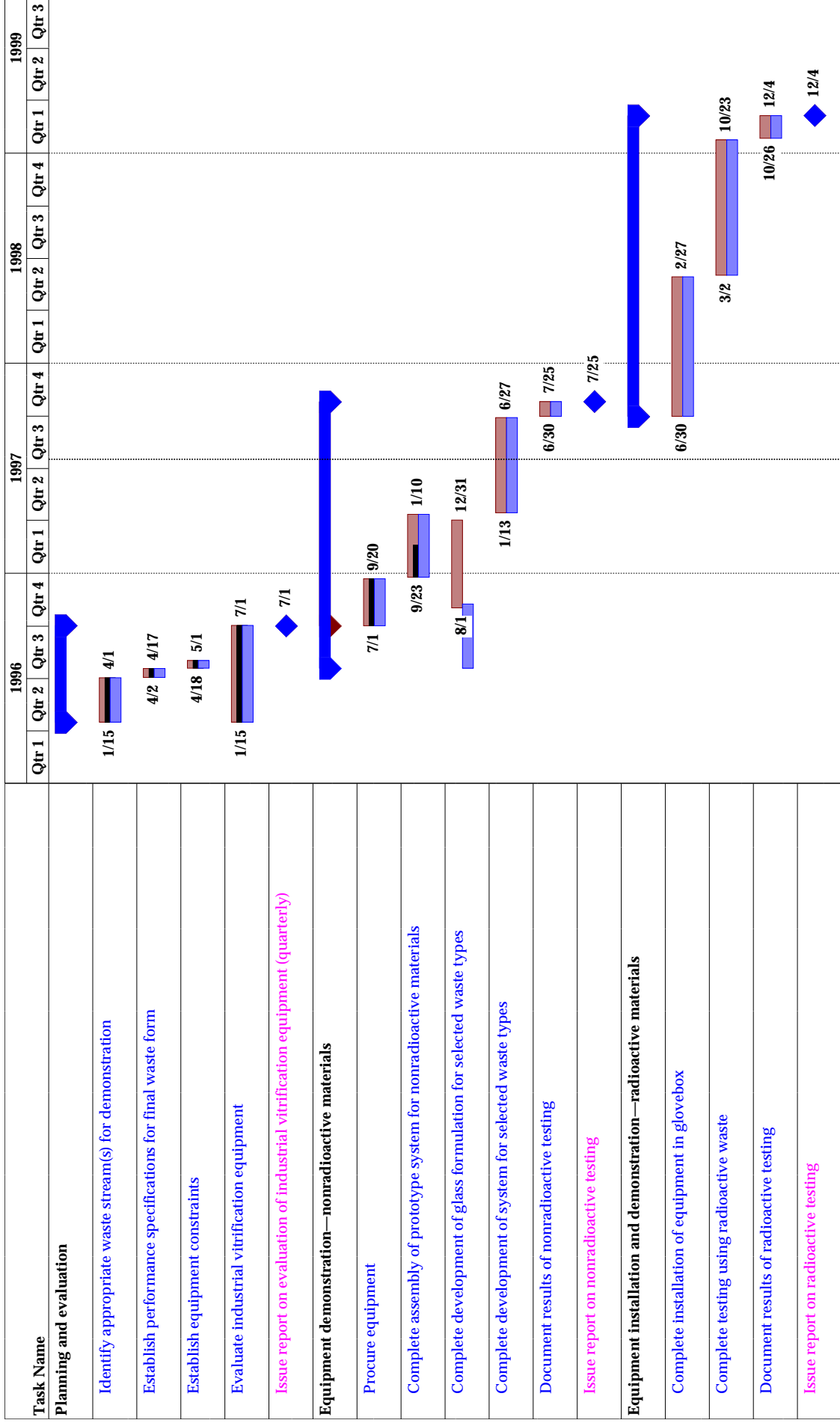
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# Vitrification



Task  
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